Studies On The Consequences of Discrete Symmetry Violations in Atoms

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by

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Under the Supervision of

Angom Dilip Kumar Singh, Associate professor Physical Research Laboratory, Ahmedabad

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UDAIPUR

Year of submission 2011

Declaration

I hearby declare that this thesis entitled 'Studies On The Consequences of Discrete Symmetry Violations in Atoms' is the result of the investigations carried out by me at the Physical Research Laboratory, Ahmedabad under the guidance and supervision of Dr. Angom Dilip Kumar Singh. This thesis has not been submitted for the award of any degree, diploma, associateship, fellowship, etc., in any university or institute.

Best effort has been put to acknowledge, whenever needed, the findings of other investigators. However, any omission which might have occurred by oversight or error in the judgment is politely regretted.

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Certificate

I feel great pleasure in certifying that the thesis entitled 'Studies On The Consequences of Discrete Symmetry Violations in Atoms' embodies a record of the results of investigations carried out by Brajesh Kumar Mani under my guidance. I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

He has completed the residential requirement as per rules.

I recommend the submission of thesis.

Date : Jan 06, 2011

Dr. Angom Dilip Kumar Singh, Associate professor Physical Research Laboratory, Ahmedabad. (Thesis Supervisor) Dedicated to,

My Grandmother, Smt. Sotiya Devi

&

My Parents, Sri. Kapildev and Smt. Ramrajee Devi

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	(1b), two-body (2b), Hermitian conjugate of one-body (1bhc)	
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	values listed are in units of $i \times 10^{-11} \mu'_W$.	127

Abstract

The parity non-conservation (PNC) in atoms arises mainly due to the weak interaction between nucleus and the electrons. The first theoretical prediction of large parity violation in heavy atomic systems was give by M. A. Bouchiat and C. Bouchiat in 1974. They showed that the PNC effects in heavy atoms or ions scale as cube of the atomic number of the atom. Following their prediction, PNC has been confirmed in several atoms such as, Cs, Bi, Pb, Tl and Yb. Results from the atomic-parity-violation (APV) experiments in combination with the precise theoretical data can be an important probe of physics beyond the Standard model of particle physics.

The most precise measurement to date, with an accuracy of 0.35%, is performed by Wiemen and collaborators [C. S. Wood, *et al.* Science **275**, 1759 (1997).] in atomic Cs. The precise theoretical calculation, however, is also done for the same atom with an accuracy of 0.5% [V. A. Dzuba, V. V. Flambaum, and J. S. M. Ginges, Phys. Rev. D **66**, 076013 (2002).]. It must be mentioned that unlike the Cs which resembles a relatively simple electronnucleus structure, the precise calculation of the PNC observable in some of the complicated structured atomic systems, such as Yb, is nontrivial. However, for this atom PNC experiment is in progress. In the case of atomic Yb for example, the theoretical and experimental uncertainties are approximately about 15-20% and 14%[K. Tsigutkin, *et al.* Phys. Rev. Lett. **103**, 071601 (2009).], respectively. The current thesis work is theoretically aimed to develop the atomic many-body methods for precise, perhaps to the level commensurate with Cs, calculation of PNC observables in these systems.

The coupled-cluster theory (CCT) is proven to be one of the accurate atomic many-body methods for structure calculations of the many-electron atoms. As a part of the thesis work, we have developed the CCT based methods for closed-shell, one-, and two-valence atoms. To test the quality of the atomic wave functions hence calculated, we examine several atomic properties, for example correlation energy and dipole polarizibility at the closed-shell sector and excitation energy, hyperfine structure constants, and electric dipole transition reduced matrix elements at one- and two-valence sectors. The PNC observable E1PNC is then calculated, for many transitions, in the case of one-valence systems, Cs, Fr, Ba⁺ and Ra⁺, and in the two-valence system, Yb.

Chapter 1 Introduction

Symmetry is the preservation of a physical quantity, which could be scalar, vector, or tensor, under a transformation about a point, a line, or a plane. Objects in nature exhibit various symmetries. According to Weyl, An object is said to be symmetrical if certain transformation associated with an operation leaves the object unchanged. For example, a sphere is symmetric when rotated around an axis passing through its center. similarly, an equation describing a systems is said to be invariant when its form remains unchanged after a given transformation. Following Noether's theorem, a continuous symmetry operation in nature is associated with a invariant quantity. Often, invariance is also referred to as conservation and in this thesis we use the two interchangeably and mean the same. An example is, linear momentum is the invariant quantity associated with translation in space (Δx) .

Depending on the associated transformations, symmetries can be classified in to two broad categories

- continuous and
- discrete.

Continuous symmetries can undergo infinitesimal transformations and finite transformations are results of a finite number of infinitesimal transformations. For example, rotation is a continuous symmetry parametrised by the angle of rotation and we can define rotation by an infinitsimaly small angle. The other important continuous symmetry transformations in nature are, translation in space, translation in time, etc. Discrete symmetries, on the other hand, do not have an associated infinitesimal transformations. The transformation parameter are allowed to have only discrete finite values. For example, symmetries associated with crystals are discrete in nature. There are three fundamental discrete symmetries in the nature. These are, the time reversal(T), space inversion or parity (P), and the charge conjugation (C). Out of these, the effects of parity violation in atomic systems is the main objective of this thesis work.

1.1 Parity or space inversion symmetry

In quantum mechanics, the concept of parity arises when we examine the form of a wave function under the operation of inversion of coordinates, namely $x \to -x$, $y \to -y$ and $z \to -z$. Parity transformation is represented by the operator \hat{P} and it has eigenvalues $\eta = \pm 1$. The even (odd) parity wave functions correspond to parity eigenvalue 1 (-1). In the context of atoms, the Hamiltonian H of an atom transforms under the parity operation as

$$H_p = PHP^{-1}. (1.1)$$

The atomic Hamiltonian is invariant under the above transformation if it satisfies

$$H = H_p = PHP^{-1}. (1.2)$$

This implies that

$$[H, P] = 0. (1.3)$$

This is true when H includes only electromagnetic interactions between the sub-atomic particles. The invariance is, however, violated when the atomic Hamiltonian incorporates parity nonconserving (PNC) weak interactions between the subatomic particles. The total Hamiltonian may then be written as

$$H_{\rm A} = H + H_{\rm PNC},\tag{1.4}$$

where H_{PNC} is the PNC interaction Hamiltonian described in the subsequent sections of the chapter. The total Hamiltonian, then no longer commute with parity operator

$$[H_{\rm A}, P] \neq 0.$$
 (1.5)

Consequently, the eigen states of H_t do not have definite parity, and are not parity eigenstates.

1.2 Parity non-conservation in nature

Until 1950, like conservation of energy and momentum, parity of a system or a process was believed to be conserved. First indication that parity may not be conserved in certain process came in 1950 while solving the theta-tau puzzle. The theta and tau mesons were discovered in the cosmic ray by C. F. Powell. These two particles were turned out to be indistinguishable other than their mode of decay. The former one was found to be disintegrating into two pions, however the later one into three. In 1956, T. D. Lee and C. N. Yang [1] predicted that it could be because of the violation of the parity in the decay process. And later they proposed several experimental schemes to test the non-conservation of parity in weak interactions. The prediction of Lee and Yang was verified when C. S. Wu [2] and collaborators studied the beta decay of Cobalt-60 in 1957. In the experiment, they lowered the temperature of cobalt atoms to about 0.01K and polarized the nuclear spins along a direction with external field. The angular distribution of the electron emitted during the beta decay were then measured. If parity is conserved, equal numbers of electrons should be emitted parallel and anti-parallel to the nuclear spin. But they measured more electrons in the direction opposite to the nuclear spin. This is a clear indication of parity non-conservation.

1.3 Parity non-conservation in atoms

Much before the formulation of a unified gauge theory of electromagnetic and weak interactions, Zel'dovich [3] had suggested the possibility of nonconservation of parity in atoms due to weak interaction between the electron and nucleon. He calculated the observable effects in atomic hydrogen using optical rotation and predicted the effects rather small for experimental observation. Despite the initial investigations of Zel'dovich [3] and Curtis-Michel [4], the possibility of parity violations in radiative transitions of atoms was not accepted. One important reason is, until 1970s all the processes involving weak interactions were believed to involve exchange of the electric charge between the interacting particles. It was therefore concluded that the weak interaction and its associated parity violation is not of the relevant to the atoms.

The important break through was the prediction of neutral weak current as a consequence of electroweak unification. The unification was achieved through the pioneering works of Abdus Salam [5], Sheldon Glashow [6] and Steven Weinberg [7], for which they were awarded the Nobel Prize of Physics in 1979. It provides a unified description of the electromagnetic and weak interactions. One outcome of the unification is the prediction of a neutral gauge boson Z^0 which mediates neutral weak current. These new developments in weak interaction physics renewed interest in the physics of parity violation in atomic systems. And the first theoretical analysis of PNC in atoms was reported in 1974 by Bouchiat and Bouchiat [8]. They predicted that in the heavy atoms, due to the stronger nuclear potential the probability distribution of electrons within nucleus is larger and enhances the Z^0 exchange between the electrons and nucleons. The effect scales as the cube of the atomic number [9] of the atoms. Following the theoretical prediction, PNC in atoms was investigated by several experimental groups. As a result PNC in atoms was observed in several heavy atoms like Cs [10], Bi [11], Pb [12], Tl [13, 14] and Yb [15].

A	
2009	Enhanced PNC was confirmed in Yb by Budker and collaborators at B- erkeley.
1997	Most precise experiment in Cs was performed by Weiman and collab- orators at Boulder.
1995	PNC was seen in Cs, Tl, Bi and Pb by groups at Boulder, Oxford, O- xford and Seattle respectively.
1979	PNC in atomic Tl was observed by Commins and collaborators at B-erkeley.
1978	PNC was observed in Bi by L. M. Barkov and M. S. Zolotrov at No- vosibirsk.
1974	M. A. Bouchiat and C. Bouchiat theoretically showed that the effects grow as faster than Z^3 and, can therefore be experimentally observed in heavy atoms.
1959	Ya. B. Zeldovich predicted the existence of PNC in atoms. He concl- uded that the effects are too small to be observed.

Figure 1.1: Schematic of the various achievements of PNC in atoms.

1.3.1 Theoretical calculations of atomic PNC

The observable quantity arising from PNC in atoms is the parity-violating electric dipole transition amplitude (E1PNC). It is expressed in terms of a parameter, such as the nuclear weak charge Q_W and parity odd nuclear moment μ'_w , these are extracted from the results of APV experiments after combining with the theoretical results. In the absence of PNC interaction, atomic states have definite parity, and the electric dipole transition amplitude (E1) between states of same parity is zero. The PNC interactions, however, mixes atomic states of opposite parities and introduces a finite transition amplitude, E1PNC, between states of same parity. In the subsequent chapters of the thesis we provide detailed expressions of E1PNC using relevant atomic many-body methods.

Most of the accurate calculations to date have been carried out to study the effects of nuclear spin-independent (NSI) part of the PNC. Some important ones are listed in Table. 1.1. Apart from those mentioned in the table, there are

Atom	Transition	Theoretical	Reference
		Uncertainty	
205 Tl	$6P_{1/2} \longrightarrow 6P_{3/2}$	2.5 - 3%	[16, 17].
$^{205}\mathrm{Tl}$	$6P_{1/2} \longrightarrow 7P_{1/2}$	6%	[16].
$^{208}\mathrm{Pb}$	${}^{3}P_{0} \longrightarrow {}^{3}P_{1}$	8%	[18].
$^{209}\mathrm{Bi}$	${}^3S_{3/2} \longrightarrow {}^2D_{3/2}$	11%	[18, 19].
$^{209}\mathrm{Bi}$	$^{3}S_{3/2} \longrightarrow ^{2}D_{5/2}$	15%	[20].
$^{133}\mathrm{Cs}$	$6S_{1/2} \longrightarrow 7S_{1/2}$	0.5%	[21].
^{133}Cs	$6S_{1/2} \longrightarrow 7S_{1/2}$	< 1%	[19, 22, 23]

Table 1.1: Summary of the NSI E1PNC theoretical calculations.

few other important recent studies on NSI E1PNC. These are the studies of Sahoo and collaborators [24, 25] for Ba⁺, [26] for Ra⁺ and Pal and collaborators [27] for Ra⁺. Unlike the NSI part, the nuclear spin-dependent (NSD) part of PNC on the other hand has not been studied in detail and there are few results in literature. Some of the important ones are Singh [28], and Porsev and collaborators [29] for Yb, Johnson and collaborators [30] for Cs, Porsev [31] for Fr, and Singh and collaborators [32, 33] for Ba⁺ and Ra⁺. In a very recent work, Sahoo and collaborators [34] have examined several transition reduced matrix elements for different isotopes of Ba⁺ and Ra⁺ ions.

As its evident from the Table. 1.1, except for the atomic Cs theoretical results are not very accurate. Hence these need to be calculated using more accurate atomic many-body theories, as there has been enormous improvements in computational resources and many-body methods applicable to atoms in the last few years. However, the current thesis focuses more on the NSD part of the PNC violation where there is a need of precise theoretical data in experimentally important systems like atomic Yb.

1.3.2 Sources of PNC in atoms

There are two important sources of PNC in atoms [28, 29]. These are the

- neutral weak current interactions between the nucleons and electrons through the exchange of Z^0 boson.
- electromagnetic interaction between the nuclear anapole moment (NAM) of the nucleus and the electrons [10].

The anapole moment, introduced by Zel'dovich [35], is an odd parity electromagnetic moment arising from the toroidal current distribution within the nucleus. In other words, the parity non-conserving nuclear forces create helical spin and magnetic moment distribution inside the nucleus lead to nuclear anapole moment. For a point like nucleus the contribution from the anapole moment to the nuclear vector potential is given by the expression

$$\boldsymbol{A}_{\text{anapole}} = \boldsymbol{a}\delta(r), \tag{1.6}$$

where the anapole moment

$$\boldsymbol{a} = -\pi \int \boldsymbol{j}(r)r^2 d^3r. \tag{1.7}$$

Here, $\mathbf{j}(r)$ is the current density inside the nucleus. For details on the anapole moment one can see the review article [36].

1.3.3 Z^3 dependence in heavy atoms

As mentioned earlier, in 1974 Bouchiat and Bouchiat [8, 9, 37] predicted that PNC effects in atoms scales as Z^3 . To understand the Z^3 scaling, consider the PNC electron-nucleus potential expressed in the form [8],

$$V_{\rm pv} = \frac{Q_{\rm W}G_{\rm F}}{4\sqrt{2}} \left[\delta^3(\boldsymbol{r}_e) \frac{\boldsymbol{\sigma} \cdot \boldsymbol{v}_e}{c} + \text{h.c.} \right].$$
(1.8)

Where, $Q_{\rm W}$ and $G_{\rm F}$ are the weak nuclear charge and the Fermi coupling constant respectively, associated with the weak interaction between the nucleus and electrons. σ_e and v_e are the spin and velocity of the electron respectively. The delta function here signifies that unlike the Coulomb potential, the electron-nucleus interaction is short range in comparison to the atomic size. The origin of each Z dependence are described in the following paragraphs.

First, one factor of Z arises from the weak charge of the nucleus. It is defined as

$$Q_{\rm W} = -N + Z(1 - 4\sin^2\theta_{\rm w}), \tag{1.9}$$

where N and Z are the number of neutrons and protons respectively in the nucleus and, $\theta_{\rm w}$ is the Weinberg angle. The experimentally measured value of $\sin^2 \theta_{\rm w}$ is ≈ 0.23 . Hence from Eq. (1.9)

$$Q_{\rm W} \approx -N \ge Z,\tag{1.10}$$

for most of the heavy stable nuclei $N/Z \ge 1$.

Second, one Z factor arises from the helicity factor $\boldsymbol{\sigma} \cdot \boldsymbol{v}_e/c$ in Eq. (1.8). Within the nuclear region the electronic velocity v_e is proportional to the nuclear charge Z. Finally, another Z factor is attributed to the delta function appearing in Eq. (1.8). The consequence of having delta function is that, only the electronic wave function which has non zero probability within the nucleus contributes the to the PNC observables. For example, the most dominant contributions are from $s_{1/2}$ and $p_{1/2}$ orbitals.

1.4 PNC interaction Hamiltonian

The PNC electron-nucleus interaction Hamiltonian density of an atom in second quantized form is expressed as

$$\mathcal{H}_{PNC} = G_F(C_1 \overline{\psi}_e \gamma_\mu \psi_e \overline{\psi}_n \gamma_5 \gamma_\mu \psi_n + C_2 \overline{\psi}_e \gamma_5 \gamma_\mu \psi_e \overline{\psi}_n \gamma_\mu \psi_n).$$
(1.11)

In the above equation $G_{\rm F}$ is the Fermi coupling constant and it gives a measure of the weakness of the interaction. In atomic units it has the value 2.2225 × 10^{-14} . C_1 and C_2 are electron-nucleon coupling coefficients. γ_{μ} and γ_5 are the Dirac matrices expressed as

$$\gamma_k = \begin{pmatrix} 0 & -i\sigma_k \\ i\sigma_k & 0 \end{pmatrix}, \ k = 1, 2, 3 \text{ and } \gamma_5 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix},$$
 (1.12)

I here is the nuclear spin quantum number. The first term in Eq. (1.11) is the nuclear-spin dependent (NSD) part of the PNC interaction Hamiltonian, as it has the vector electron $(\overline{\psi}_e \gamma_\mu \psi_e)$ and the axial vector nucleus $(\overline{\psi}_n \gamma_5 \gamma_\mu \psi_n)$ currents. The second term on the other hand, has the vector nucleus $(\overline{\psi}_n \gamma_\mu \psi_n)$ and the axial vector electron $(\overline{\psi}_e \gamma_5 \gamma_\mu \psi_e)$ currents and hence represents the nuclear spin-independent (NSI) part of the PNC interaction Hamiltonian. As vector changes sign under the parity operation but the axial vector does not, and hence the product of two violates the parity transformation. From Eq. (1.11), the total PNC Hamiltonian is then

$$H_{\rm PNC} = \int \mathcal{H}_{\rm PNC} d^3 r. \tag{1.13}$$

In the subsequent sections we provide expressions for the NSD and NSI PNC interaction Hamiltonian's separately.

1.4.1 NSD-PNC interaction Hamiltonian

From Eq. (1.11), consider the first term

$$G_{\rm F}C_1\bar{\psi}_e\gamma_\mu\psi_e\bar{\psi}_n\gamma_5\gamma_\mu\psi_n = -G_{\rm F}C_1\psi_e^{\dagger}\gamma_0\gamma_\mu\psi_e\psi_n^{\dagger}\gamma_0\gamma_\mu\gamma_5\psi_n,\qquad(1.14)$$

we have used the anticommutation relation $\{\gamma_5, \gamma_\mu\} = 0, \ \mu = 0, 1, 2, 3$, and the expression $\bar{\psi} = \psi^{\dagger} \gamma_0$. Using Eq. (1.13), the total NSD-PNC Hamiltonian is

$$H_{\rm PNC}^{\rm NSD} = -G_{\rm F}C_1 \int \psi_e^{\dagger} \gamma_0 \gamma_\mu \psi_e \psi_n^{\dagger} \gamma_0 \gamma_\mu \gamma_5 \psi_n d^3 r.$$
(1.15)

Expanding this equation for all values of μ , we get

$$H_{\rm PNC}^{\rm NSD} = -G_{\rm F}C_1 \int \left[\psi_e^{\dagger}\gamma_0\gamma_0\psi_e\psi_n^{\dagger}\gamma_0\gamma_0\gamma_5\psi_n + \psi_e^{\dagger}\gamma_0\gamma_k\psi_e\psi_n^{\dagger}\gamma_0\gamma_k\gamma_5\psi_n\right] d^3r. (1.16)$$

Consider the first term, $\mu = 0$, and treat the nuclear part non-relativistically, we then get

$$\int \psi_e^{\dagger} \gamma_0 \gamma_0 \psi_e \psi_n^{\dagger} \gamma_0 \gamma_0 \gamma_5 \psi_n d^3 r = \int \psi_e^{\dagger} \psi_e \psi_n^{\dagger} \gamma_5 \psi_n d^3 r$$
$$= \int \left(\begin{array}{c} P_n \chi_{\kappa_n m_n} \\ 0 \end{array} \right)^{\dagger} \left(\begin{array}{c} 0 & I \\ I & 0 \end{array} \right) \left(\begin{array}{c} P_n \chi_{\kappa_n m_n} \\ 0 \end{array} \right) \psi_e^{\dagger} \psi_e d^3 r = 0, \quad (1.17)$$

here we have used the relations $\gamma_0^2 = 1$. Similarly, for the remaining terms $\mu = 1, 2, 3$, which are the spatial components we get

$$\int \psi_e^{\dagger} \gamma_0 \gamma_k \psi_e \psi_n^{\dagger} \gamma_0 \gamma_k \gamma_5 \psi_n d^3 r = \int \psi_e^{\dagger} i \alpha_i \psi_e \psi_n^{\dagger} i I_i \psi_n d^3 r$$

where we have used the relations $\gamma_0 \gamma_i = i\alpha_i$ and $\gamma_0 \gamma_i \gamma_5 = iI_i$. From Eqs. (1.17), (1.18) and (1.15), the NSD PNC interaction Hamiltonian in the first quantized form is

$$H_{\rm PNC}^{\rm NSD} = \frac{G_{\rm F}\mu'_W}{2\sqrt{2}I} \sum_i \vec{\alpha}_i \cdot \vec{I}\rho_{\rm N}(r), \qquad (1.18)$$

where μ'_W is the weak nuclear moment of the nucleus and $\rho_N(r)$ is the nuclear density. The weak nuclear moment is expressed in terms of the neutron and proton numbers $\mu'_W = 2(ZC_{1p} + NC_{1n})$, where C_{1p} and C_{1n} are respectively the vector electron and the axial vector nucleon coupling coefficients.

The parameter μ'_W introduced here has the combined effects of three parity violating NSD-PNC contributions: interaction between nuclear anapole moment and electrons; Z^0 exchange between electron and nucleons; and combined effect of perturbation of the NSI contribution and hyperfine interaction. Among these, the first is the most dominant, however, experimentally it can not be distinguished from the effects of neutral weak currents. This must be accounted for while extracting the anapole moment from atomic measurements. Using the above arguments we can write in Eq. (1.18)

$$\mu'_W = (-1)^{I+1/2-l} \left(\frac{I+1/2}{I+1}\right) \mu_a + \mu_2 + \mu_{Q_W}, \qquad (1.19)$$

where, the constant μ_a represents the contribution from anapole moment, the constant μ_2 accounts for the contribution from the neutral weak currents, and the last term μ_{Q_W} corresponds to the interference between the NSI and the hyperfine interaction. l is the orbital angular momentum of the unpaired nucleon.

1.4.2 NSI PNC interaction Hamiltonian

The NSI part of H_{PNC} is the most dominant source of PNC effects in atoms. At the nuclear level, the associated parameter of the NSI-PNC interaction is the weak charge of the nucleus Q_W and the interaction Hamiltonian is [8]

$$H_{\rm PNC}^{\rm NSI} = \frac{G_{\rm F}}{2\sqrt{2}} Q_W \sum_i \gamma_5 \rho_N(r_i), \qquad (1.20)$$

where the weak charge Q_W of the nucleus is

$$Q_W = 2(ZC_{2p} + NC_{2n}). (1.21)$$

Here, Z and N are the number of protons and neutrons respectively. And C_{2p} and C_{2n} are the vector and axial coupling constants of the nucleon and electron respectively. As mentioned earlier, $\rho_N(r_i)$ is the nuclear density.

1.5 Objectives of the current study

The standard model (SM) of particle physics is a theory of the elementary particles in nature and their interactions. It correctly predicts the existence of guage bosons, the force carriers which mediates the the strong, weak, and electromagnetic fundamental interactions. However, a hypothetical massive scalar elementary particle predicted by the SM and referred to as the Higgs boson is yet to be detected in experiments. The Higgs boson plays an important role in explaining the origin of mass. Apart from this, the SM lacks a consistent description of several observed phenomena, to mention a few

- the origin of strong CP violation,
- matter-antimatter asymmetry in the universe,
- neutrino oscillations,
- the origin and nature of dark matter and dark energy,

In the literature, these fall under the broad category of physics beyond the SM. These have motivated several extensions to the SM and these are for example supersymmetric and left-right symmetric models. One way to investigate these extended models is at the high-energy collider experiments, where new particles can be detected and study their properties. Another way to probe physics beyond the SM is with low-energy atomic experiments. The experimental results when combined with high precision atomic theory calculations provide estimates of parameters in SM. Any deviation from the predictions of SM is indicative of new physics.

The current thesis work is motivated to contribute to the new physics by developing atomic many-body theory methods to carry out high precision atomic theory calculations. For the computational results, the focus of the work is the PNC of Yb [38, 39, 40, 28, 41, 15] and in particular, the NSD-PNC component. The PNC effects of atomic Yb are reported to be almost ≈ 100 times larger than the most precisely studied case of atomic Cs [10]. Apart form the previously mentioned implication to the new physics, there are several other important implications of the proposed work. As an application of the theoretical methods developed, we also examine the spectroscopic properties of atoms. A major part of the new atomic many-body methods developed are based on the relativistic coupled-cluster theory.

1.6 Outline of the chapters

The chapters in the remaining part of the thesis are briefly outlined in this section.

The second chapter, Atomic many-body perturbation theory (MBPT), provides a basic description of atomic structure calculations. Towards the end of the chapter, MBPT is applied to calculate energy and E1PNC. The first section of chapter discusses the many-electron relativistic Hamiltonian and relations between different wave functions, the spin-orbitals, the configuration state functions (CSF) and the atomic state functions (ASF). The concepts in MBPT based on Rayleigh-Schroedinger perturbation theory are described in Sec. II. The application MBPT to the closed- and open-shell atoms are discussed in the Sec. III and IV, respectively. In these sections, the details of the calculations of the correlation and excitation energies are provided. Application of MBPT to study PNC in atoms are discussed in the Sec. V and results are presented in the section.

The third chapter, *Perturbed configuration interaction (PCI)*, provides an important scheme to overcome the computational difficulty of diagonalizing two very large matrices in configuration interaction (CI). The first section is a brief description of the CI method and its application to calculate E1PNC. The next section forms the core of the chapter and the PCI method is examined in detail. It gives the E1PNC expression within PCI and demonstrates the advantage of PCI over CI. Sec. III deals with the application to the atomic Yb and results are presented in the last section of the chapter.

In the fourth chapter, *Coupled-cluster theory for closed-shell and one*valence atoms, we deal with the developments and implications of most efficient atomic many-body method, the coupled-cluster. This chapter is comprise of four sections. The CC equations of closed-shell systems are derived in the first section of the chapter. The properties calculation for closed-shell systems using CC wave function is also discussed in the same section. Sec. II deals with the method in the context of one-valence atoms. The coupled-cluster working equations are derived, and application to the excitation energy calculation is briefed. The properties calculations for one-valence atoms, in particular the hyperfine structure constants (HFS) and the electric dipole transition amplitudes (E1), are discussed in Sec. III. A scheme for all-order properties calculation is also described in the same section. This scheme enable us to include higher orders of closed-shell cluster operators in the properties calculation. Results obtained based on CC theory are presented in the last section.

The fifth chapter, *Coupled-cluster theory for two-valence atoms*, is the heart of the thesis. In this chapter we deal with CC theory for two-valence atomic systems. This is broadly classified in to four sections. Sec. I provides an overview of the multi-reference CCT followed by *complete* and *incomplete* model spaces. The coupled-cluster working equations using exponential ansatz and the Bloch equation are derived in Sec. II of the chapter. The properties calculations using CC method are discussed in Sec. III. In particular, we provide working equation and diagrammatic analysis for the calculation of HFS constants and E1 transition matrix element. The results calculated using CC method are presented and analyzed in last section of the chapter.

The sixth chapter, *Coupled-cluster theory with PNC perturbation*, is to account for PNC perturbation in atomic systems using the coupled-cluster method. In the first section we consider closed-shell atoms in the PNC perturbation. The perturbed CC equations for the same are are derived. We also describe the scheme for properties, in particular, the dipole polarizibility, calculation. The perturbed CC equation for one-valence atoms are discussed in Sec. II. As an application we implement it for the E1PNC calculation, which is also given in the same section. Sec. III considers two-valence atoms in the PNC perturbation. The perturbed CC equations for the same are derived, and is also applied to E1PNC calculation. Results are presented in the last section of the chapter.

The last chapter, Summary of the E1PNC results and future directions, entangle the outcomes of the thesis. This chapter is divided into two sections. Sec. I present the E1PNC results calculated using the methods which are developed as the part of the thesis work for one-valence systems. The same for two-valence systems are presented in Sec. II.

Chapter 2

Atomic many-body perturbation theory

The many-body perturbation theory (MBPT) is an approach based on the *perturbation* procedure to account for electron-electron interactions in manybody systems. In atomic physics it was first introduced by Kelly [42] in 1969 and later proved as a powerful and suitable method for atomic and molecular calculations. It has been applied quite successfully for correlation energy calculation to the several atomic systems [43, 44, 45]. It is, however, not practical to proceed beyond the third order as the number of terms proliferate rapidly with the order of perturbation. At fourth order, there are large number of terms and calculations are unmanageable. Perhaps in future, a combination of symbolic manipulation and advances in computational many-body techniques may remedy the complications. The method, however, is indispensable in optimizing and testing the quality of the single-electron basis functions. In addition, it is invaluable as a benchmark to test and validate other atomic many-body theories.

The chapter is organized as follows. In Section.II we give an overview of the method and described the basic idea followed. The next section deals, in brief, with very general and widely applicable perturbation scheme, the Rayleigh-Schroedinger perturbation scheme, followed by the description of the Generalized Bloch equation. Section.IV. is about the application of MBPT for the correlation energy calculation in the case of closed- and open-shell atomic systems. In the two-valence atoms case the construction of the effective Hamiltonian matrix and its diagnolization in the jj coupled states is elaborated. And the last section describes the scheme to calculate the E1PNC using MBPT wave function.

2.1 Relativistic atomic theory

To obtain precise results it is necessary to include effects of relativity in the atomic many-body calculations. It is particularly important in high Zatoms/ions as relativistic effects are large. The Dirac-Coulomb Hamiltonian [46], $H^{\rm DC}$, is an appropriate choice to incorporate relativistic effects. For an N-electron atom or ion

$$H^{\rm DC} = \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta - 1)c^2 - \frac{Z}{r_i} \right] + \sum_{i < j} \frac{1}{r_{ij}}, \qquad (2.1)$$

where, α and β are the Dirac matrices. The first term in above equation is the kinetic energy of the electrons. The third term is the nuclear potential, and the last term represents Coulomb interactions of electrons. As the name suggests, $H^{\rm DC}$ includes all possible Coulomb interactions, and neglects the magnetic interactions. It satisfies the Schroedinger equation

$$H^{\rm DC}|\Psi_i\rangle = E_i|\Psi_i\rangle,\tag{2.2}$$

where $|\Psi_i\rangle$ is the exact wave function usually referred as the atomic state function (ASF). And, E_i is the exact energy of the atomic system considered.

2.1.1 Dirac-Hartree-Fock theory

Hydrogen atom, which has only one electron along with the nucleus, is a twobody system and is exactly solvable. However, the other atoms or ions with two or more electrons are not exactly solvable. This is on account of of the electron-electron Coulomb interaction $\sum_{i < j} \frac{1}{r_{ij}}$ in atomic Hamiltonian.

To solve Eq. (2.2) we invoke the independent-particle model, which assume each electron to move independently of others in an average potential arising from the nucleus and other electrons. The average potential from the other electrons [46, 47] is the Dirac-Hartree-Fock central potential

$$u_{\rm DF}(\boldsymbol{r}_i)|i\rangle = \sum_{a}^{\rm occ} \left[\langle a|\frac{1}{r_{12}}|ia\rangle - \langle a|\frac{1}{r_{12}}|ai\rangle \right], \qquad (2.3)$$

where, *i* represents any orbital (core, valence, or virtual) and *a* represents only the occupied orbitals. The first and second terms on right hand side are the *direct* and *exchange* terms respectively. It is evident that *direct* and *exchange* cancels when i = a and avoids self interaction. We can then rewrite

$$H^{\text{DC}} = \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_{i} \cdot \boldsymbol{p}_{i} + (\beta - 1)c^{2} - \frac{Z}{r_{i}} + u_{\text{DF}}(\boldsymbol{r}_{i}) \right] + \sum_{i < j}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} u_{\text{DF}}(\boldsymbol{r}_{i}),$$

= $H_{0} + V_{\text{es}}.$ (2.4)

Where, H_0 is the solvable part of H^{DC} , conventionally referred as zeroth order Hamiltonian. It can further be expressed as the sum of single particle operators

$$H_0 = \sum_{i}^{N} h_{\rm DF}(i),$$
 (2.5)

where

$$h_{\rm DF}(i) = c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 - \frac{Z}{r_i} + u(\boldsymbol{r}_i), \qquad (2.6)$$

is the Dirac-Fock operator. The remaining part of the electron-electron Coulomb interaction

$$V_{\rm es} = \sum_{i < j}^{N} \frac{1}{r_{ij}} - \sum_{i} u_{\rm DF}(\boldsymbol{r}_i), \qquad (2.7)$$

is the residual Coulomb interaction [46, 47] or the perturbative part of H^{DC} . The purpose of any atomic many-body theory is to account for this term as accurately as possible. And, that is the objective of the many-body atomic calculations.

2.1.2 Single-electron wave function

The Dirac-Fock operator, introduced in Eq. (2.5), satisfies the eigenvalue equation

$$h_{\rm DF}(i)|\psi_i\rangle = \epsilon_i |\psi_i\rangle,\tag{2.8}$$

where, $|\psi_i\rangle$ and ϵ_i are the single electron wave function and energy respectively. These are obtained from a self consistent field calculations of the single particle equations. The relativistic orbitals are of the form

$$\psi_{n\kappa m}(\boldsymbol{r}) = \frac{1}{r} \left(\begin{array}{c} P_{n\kappa}(\boldsymbol{r})\chi_{\kappa m}(\boldsymbol{r}/r) \\ iQ_{n\kappa}(\boldsymbol{r})\chi_{-\kappa m}(\boldsymbol{r}/r) \end{array} \right), \qquad (2.9)$$

where, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small component radial wave functions, κ is the relativistic total angular momentum quantum number and $\chi_{\kappa m}(\mathbf{r}/r)$ are the spinor spherical harmonics defined as

$$\chi_{\kappa m}(\boldsymbol{r}) = \sum_{\sigma=\pm\frac{1}{2}} \langle lm - \sigma, \frac{1}{2}\sigma | jm \rangle Y_l^{m-\sigma}(\theta, \phi) | \sigma \rangle.$$
(2.10)

The term $\langle lm - \sigma, \frac{1}{2}\sigma | jm \rangle$, in the above equation, is a Clebsch-Gordan coefficient and $Y_l^{m-\sigma}(\theta, \phi)$ and $|\sigma\rangle$ are the spherical harmonics and spin basis functions respectively. The radial components of the wave function is further expressed as the linear combination of Gaussian like functions, referred to as Gaussian type orbitals (GTOs) [48, 49]

$$P_{n\kappa}(r) = \sum_{p} C^{L}_{\kappa p} g^{L}_{\kappa p}(r),$$
$$Q_{n\kappa}(r) = \sum_{p} C^{S}_{\kappa p} g^{S}_{\kappa p}(r).$$
(2.11)

The index p runs over the number of the basis functions. For large component

$$g_{\kappa p}^L(r) = C_{\kappa i}^L r^{n_\kappa} e^{-\alpha_p r^2}, \qquad (2.12)$$

here n_{κ} is an integer. And the small components are related to the large component through the kinetic balance condition

$$g_{\kappa p}^{S}(r) = C_{\kappa i}^{S} \left[\frac{d}{dr} + \frac{\kappa}{r} \right] g_{\kappa p}^{L}(r).$$
(2.13)

The exponents in the above expression follow the general relation

$$\alpha_p = \alpha_0 \beta^{p-1}. \tag{2.14}$$

Where, the parameters α_0 and β are optimized for an atom to provide good description of the atomic properties.

2.1.3 Slater determinants, CSFs and ASFs

Solving the Dirac-Hartree-Fock equation, Eq. (2.8), we obtain a set of orbitals $\{|\psi_i\rangle\}$, and the corresponding eigenvalues $\{\epsilon_i\}$. From these we can construct a set of many-electron wave functions. However, to satisfy Pauli's exclusion principle, the many-electron wave function must be antisymmetric with respect to interchange of coordinates. Slater determinantal wave functions satisfy this condition [46, 47, 50] and for an N-atom

$$D(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = \begin{vmatrix} \psi_a(\mathbf{r}_1) & \psi_b(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_a(\mathbf{r}_2) & \psi_b(\mathbf{r}_2) & \cdots & \psi_n(\mathbf{r}_2) \\ \psi_a(\mathbf{r}_3) & \psi_b(\mathbf{r}_3) & \cdots & \psi_n(\mathbf{r}_3) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_a(\mathbf{r}_N) & \psi_b(\mathbf{r}_N)e & \cdots & \psi_n(\mathbf{r}_N) \end{vmatrix} .$$
(2.15)

Slater determinants are eigen functions of the zeroth-order Hamiltonian H_0 and the corresponding eigenvalue equation is

$$H_0|D_i\rangle = E_i^{(0)}|D_i\rangle, \qquad (2.16)$$

where, $E_i^{(0)}$ is the sum of all single electron energies. The difference between the exact and the mean field energy, $\Delta E_i = E_i - E_i^0$, is the correlation energy
of the *i*th state. Here, the Slater determinants are the antisymmetrised direct product of single particle wave functions. However, H_0 commutes with J^2 , J and J_z and taking these into account, we can define many-electron states which are eigenstates of J. Such states represented as $|\gamma PJM\rangle$ are referred as configuration state functions (CSFs) and are, in general, linear combinations of the Slater determinants. Where P is the parity of the state, M is the magnetic quantum number and γ is an additional quantum number to define each CSF uniquely. From the considerations mentioned

$$J^{2}|\gamma PJM\rangle = J(J+1)|\gamma PJM\rangle,$$

$$J_{z}|\gamma PJM\rangle = M|\gamma PJM\rangle,$$

$$P|\gamma PJM\rangle = P|\gamma PJM\rangle,$$

(2.17)

here, M varies from -J to +J.

The next level of many-particle wave function is the atomic state functions (ASFs). These are the linear combinations of CSFs and general expression is

$$|\Gamma PJM\rangle = \sum_{i=1}^{n} c_{i}^{\Gamma} |\gamma_{i} PJM\rangle.$$
(2.18)

The additional quantum number Γ is defines each ASF uniquely. And c_i^{Γ} is the mixing coefficients. In the later sections we will using Eq. (2.18) in the representation

$$|\Psi_i\rangle = \sum_{j=1}^n c_j^i |\Phi_j\rangle, \qquad (2.19)$$

where j is restricted to one for closed-shell atoms.

2.2 Basics of atomic MBPT

The basic idea behind atomic MBPT is to incorporate the residual Coulomb interaction $V_{\rm es}$, defined in Eq. (2.7), systematically to higher orders in a sequence. So that the eigen value equation given in Eq. (2.2) is solved exactly. From previous descriptions, the total Hamiltonian is

$$H^{\rm DC} = H_0 + V_{\rm es}.$$
 (2.20)

The initial step of MBPT calculations is to solve the eigenvalue equation of H_0 and obtain a complete set of eigen states $\{|\Phi_i\rangle\}$. The next step is separation of $\{|\Phi_i\rangle\}$ into a model space or *P*-space, it comprises of eigen states which are best approximation to the exact atomic state. And, the *Q*-space or the complementary space, it consists of the remaining eigen states. Defining the two subspaces is straight forward in closed-shell states as P-space has only one state and it is the determinant corresponding to the configuration of the atomic state. The projection operators are

$$P = |\Phi_i\rangle\langle\Phi_i|, \text{ and } Q = \sum_{|\Phi_j\rangle\notin P} |\Phi_j\rangle\langle\Phi_j|.$$
 (2.21)

In the open-shell systems, however, the selection of P-space is tricky as several eigen states may contribute equally at the lowest approximation. Details on the choice of the model space in open-shell systems shall be discussed in later parts of the thesis. The operator P satisfies the relation

$$P|\Psi_i\rangle = |\Phi_i\rangle. \tag{2.22}$$

And the final step is to define the wave operator Ω which operates within the model space but it generates the exact atomic state

$$|\Psi_i\rangle = \Omega |\Phi_i\rangle, \tag{2.23}$$

where $|\Psi_i\rangle$, as mentioned earlier, is the exact wave function and $|\Phi_i\rangle$ is the corresponding model wave function. There are two important perturbation theories to calculate the wave operator: *Brillouin-Wigner* and *Rayleigh-Schroedinger*. Detailed discussions on these theories are given in Ref.[47, 50].

The expansion series in the Brillouin-Wigner perturbation theory require, in denominator, exact energy of the atomic states. Calculation of which is one objective of the perturbation scheme. For this reason the implementation of the theory is through self consistent schemes. This constrain the general applicability of the theory as self consistent schemes usually encounter divergences while calculating several states. As a result, the theory is appropriate for calculations involving a few atomic states.

The Rayleigh-Schroedinger perturbation theory, on the other hand, depend entirely on the eigen states and eigen values of H_0 . The wave operator of a state is well defined once the eigen value equation of H_0 is solved. And, unlike the Brillouin-Wigner theory, it can be applied to a group of states with relatively simple generalizations. The theory was first applied to N-electron systems by C. Moller and M. S. Plesset and hence, in atomic and molecular physics, it is also referred as Moller-Plesset perturbation theory. In the next section a brief description of the theory is provided, which is perhaps essential and the later sections in the thesis rely on the theory either for validation or are based on it.

2.2.1 Rayleigh-Schroedinger perturbation theory

As mentioned earlier, the exact atomic state is generated from the model space wave function by means of the wave operator. This is done iteratively through successive corrections to the model function. The wave operator, in general, can be define as

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \Omega^{(3)} + \cdots, \qquad (2.24)$$

where the superscript represents the order of perturbation. The wave operator $\Omega^{(\mu)}$ has the perturbation $V_{\rm es}$ a μ number of times. In the same way, the exact state Eq. (2.23) is

$$|\Psi_i\rangle = |\Phi_i\rangle + \lambda |\Phi_i^{(1)}\rangle + \lambda^2 |\Phi_i^{(2)}\rangle + \lambda^3 |\Phi_i^{(3)}\rangle + \cdots$$
 (2.25)

Here, λ is the perturbation parameter and indicates the order of of perturbations in each term. As we have discussed earlier as well, $|\Phi_i\rangle$ is the zeroth-order wave function and in closed-shell case is the best approximation to the exact state. And the others, $|\Phi_i^{(1)}\rangle$, $|\Phi_i^{(2)}\rangle$, and so on, are the corrections evaluated with the wave operator in Eq. (2.24).

2.2.2 Generalized Bloch-equation

The wave operator, in Rayleigh-Schroedinger perturbation theory, is the solution of the iterative equation

$$[\Omega, H_0]P = V\Omega P - \Omega P V_{\rm es} \Omega P.$$
(2.26)

This equation is referred as the generalized Bloch equation and was formulated by Lindgren in Ref. [51]. It is widely used in perturbative calculations of atomic and molecular physics, and it is a convenient starting point in the derivations of non perturbative schemes like coupled-cluster theories. Another form of the equation, suitable to calculate the order wise expansion of the wave operator in Eq.(2.24), is to rewrite it as a recurrence relation

$$[\Omega^{(\mu)}, H_0]P = QV\Omega^{(\mu-1)}P - \sum_{\nu=1}^{\mu-1} \Omega^{(\mu-\nu)}PV\Omega^{(\nu-1)}P.$$
(2.27)

The equation is solved in a sequence to obtain terms in the waver operator as a function of V to various orders. However, beyond second order algebraic evaluation of the wave operator is cumbersome and book keeping of various terms is impractical. With diagrammatic evaluation, it is fairly straight forward to calculate up to third order and simplifies calculations of selective terms in MBPT to higher orders. Two classes of diagrams occur in the diagrammatic expression of Eq. (blocheq1), namely: linked diagrams, where it possible to traverse all the interaction lines in one stroke, and unlinked diagrams, where it require more than one stroke to traverse all the interaction lines. Following linked cluster theorem [52, 53], only the linked diagrams appear in Eq. (blocheq1). More appropriately

$$[\Omega^{(\mu)}, H_0]P = \left[QV\Omega^{(\mu-1)}P - \sum_{\nu=1}^{\mu-1} \Omega^{(\mu-\nu)}PV\Omega^{(\nu-1)}P \right]_{\text{linked}}.$$
 (2.28)

Where the subscript *linked* denotes only linked diagrams are retained in the equation. Ideally, in any many-body theory only linked diagrams should appear so that the theory is size extensive. Otherwise, the theory is not size extensive and there are terms which are unphysical.

2.3 Closed-shell atomic MBPT

For closed-shell atoms or states, diagrammatically, $PV\Omega^{\nu-1}P$ in the second term of Eq. (2.28) is a closed diagram. Where closed diagrams are the ones without any free orbital lines and any term which involves a closed component is then unlinked. Hence, the re-normalization term $\Omega^{(\mu-\nu)}PV\Omega^{(\nu-1)}$ in closedshell atoms or systems is unlinked and the generalized Bloch is reduced to

$$\left[\Omega^{(\mu)}, H_0\right] = \left[V\Omega^{(\mu-1)}\right]_{\text{linked}}, \qquad (2.29)$$

where $\mu \geq 1$. This is the linked diagram equation for closed-shell atomic systems. The first order wave operator equation is

$$\left[\Omega^{(1)}, H_0\right] = \left[V\right]_{\text{linked}} = V_1 + V_2, \qquad (2.30)$$

where the one- and two-body operators (V_1 and V_2) in operator form are

$$V_1 = \sum_{ij} \{a_i^{\dagger} a_j\} \langle i | v | j \rangle, \qquad (2.31a)$$

$$V_2 = \frac{1}{2} \sum_{ijkl} \{ a_i^{\dagger} a_j^{\dagger} a_l a_k \} \langle ij | r_{12}^{-1} | kl \rangle.$$
 (2.31b)

Here, $a^{\dagger}(a)$ are creation (annihilation) operators of single particle states, respectively. The indexes i, j, k, \ldots which represent general orbitals. For the H^{DC} and partitioning of H_0 considered in this work $V_1 = u_{\text{DF}}$. Following the form of V, the general expression of the first order wave operator is

$$\Omega^{(1)} = \Omega_1^{(1)} + \Omega_2^{(1)}. \tag{2.32}$$

The subscripts in the first and second terms on the right hand side indicate level of excitations single and double, respectively. After evaluating the commutation relation in Eq. (2.30)

$$\Omega_1^{(1)} = \sum_{ap} a_p^{\dagger} a_a \frac{\langle p | v | a \rangle}{\epsilon_a - \epsilon_p}, \qquad (2.33a)$$

$$\Omega_2^{(1)} = \frac{1}{2} \sum_{abpq} a_p^{\dagger} a_q^{\dagger} a_b a_a \frac{\langle pq|v|ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q}.$$
(2.33b)

Here, indexes $a, b, c, \ldots (p, q, r, \ldots)$ represent core (virtual) orbitals. Diagrammatically, the representation of the wave operators are given in Fig. 2.1. The off diagonal matrix elements of V_1 are zero when Dirac-Hartree-Fock orbitals used in the calculations. At the first order only the two-body V_2 then has non-zero contribution.



Figure 2.1: The diagrammatic representations of the one- and two-body wave operator for the closed-shell atoms. Lines with downward (upward) arrows represent core (virtual) single particle states.

2.3.1 Correlation energy of closed-shell atoms

Consider the eigen value equation of H^{DC} in Eq. (2.2). It can be written in terms of the MBPT wave function as

$$H\Omega|\Phi_i\rangle = E_i\Omega|\Phi_i\rangle. \tag{2.34}$$

Project the equation to *model space* or reference state, we get

$$H_{\text{eff}}|\Phi_i\rangle = E_i|\Phi_i\rangle,\tag{2.35}$$

where,

$$H_{\rm eff} = PH_0P + PV\Omega P, \qquad (2.36)$$

is the effective Hamiltonian. The Eq. (2.35) is an important one, it implies that H_{eff} is defined once the wave operator Ω is calculated. The key point of calculating H_{eff} is, it operates on the model function and gives the exact eigen energy. More appropriately, one can get the exact energy as

$$E_0 = \langle \Phi_0 | H_{\text{eff}} | \Phi_0 \rangle, \qquad (2.37)$$

expectation value of H_{eff} with respect to the model function. The first term in Eq. (2.36) is the leading order contribution, $E_i^{(0)}$, to the exact eigen energy E_i . It is referred as the self-consistent field (SCF) energy. And the second term, with wave operator Ω , is the correction to $E_i^{(0)}$ referred as the correlation energy. Depending on the orders of Ω , various corrections to the energy can be calculated using second term in Eq. (2.36) and the n^{th} order energy correction, for closed-shell systems, is

$$E_i^{(n)} = \langle \Phi_i | \overrightarrow{V\Omega}^{(n-1)} | \Phi_i \rangle, \text{ for } n \ge 2.$$
(2.38)

Unlike the case of Ω diagrams, the $E_i^{(n)}$ diagrams are topologically closed. Which is natural as it is expectation of a closed-shell state.



Figure 2.2: MBPT diagrams which contribute to the second-order correlation energy.

2.3.2 Second-order correlation energy

From Eq. (2.38), the second order correlation energy is

$$E_{\rm corr}^{(2)} = \langle \Phi_0 | \overrightarrow{V\Omega}^{(1)} | \Phi_0 \rangle.$$
(2.39)

Separate the perturbation Hamiltonian and wave-operator to one- and twobody parts, as in Eq. (2.31) and (2.33),

$$E_{\rm corr}^{(2)} = \langle \Phi_0 | (V_1 + V_2) (\Omega_1^{(1)} + \Omega_2^{(1)}) | \Phi_0 \rangle.$$
(2.40)

However, as mentioned earlier, the one-body term does not contribute at the first order. The expression for $E_{\rm corr}^{(2)}$ is then reduced to

$$E_{\rm corr}^{(2)} = \langle \Phi_0 | V_2 \Omega_2^{(1)} | \Phi_0 \rangle, \qquad (2.41)$$

The diagrams which contribute to $E_{\text{corr}}^{(2)}$ arise from the contraction of V_2 with $\Omega_2^{(1)}$ such that there are no free lines. There are two diagrams which meet the conditions of no free lines and these are shown in Fig. 2.2.

2.4 One- and two-valence atomic MBPT

Application of many-body atomic theories to the open-shell atoms, in general, is not straight forward like in closed-shell atoms. There are two reasons for this. First, in addition to the core and virtual orbitals, open shell atoms/ions require a third category, the valence orbitals. This is because, the valence shells are partially filled and these have properties typical of core shells as well as the virtual shells. And second, there is lack of a priori information about the reference state or the zeroth order wave function. This is for the following reason: usually, the valence-valence correlation effects are strong in open-shell systems and states in the model space mixes very strongly. To account for this, a reference state must be linear combination of states in the model space. However, there are no simple ways to assign the coefficients of mixing. One widely often used solution is to diagonalize the effective Hamiltonian matrix within model space configurations.



Figure 2.3: Diagram showing merging of valence orbitals with cores and virtuals.

In short, for open-shell calculations, the valence must be treated either as core or virtual depending on the context. This is depicted schematically in the Fig. 2.3 and there are advantages of such a treatment while evaluating diagrams. The open-shell diagrams are equivalent to closed-shell diagrams with the core lines transformed to valence lines. The model space consist of several states or more appropriately, the calculation is multi-reference. For single-valence case, the model functions are

$$\Phi_v \rangle = a_v^{\dagger} |\Phi_0\rangle, \qquad (2.42)$$

where $|\Phi_0\rangle$ is the core part and v represents the valence electron.

Diagrammatically, the effective Hamiltonian $PV\Omega P$ is no longer a closed diagram. It may have valence orbitals as free lines and contraction with Ω is possible. In which case, the connecting line(s) must be contorted to obtain correct expressions (denominator) and a new class of diagrams, *folded* diagrams, emerge from third order onwards. This is a major departure from the diagrammatic description of closed-shell atomic MBPT. Perturbation expansions are therefore based on the equation

$$\left[\Omega^{(\mu)}, H_0\right] = \left[QV\Omega^{(\mu-1)} - \sum_{\nu=1}^{\mu-1} \Omega^{(\mu-\nu)} PV\Omega^{(\nu-1)}\right]_{\text{linked}}.$$
 (2.43)

Recollect that the second term on the right-hand side of Eq. (2.43) is absent in close-shell case.

2.4.1 Excitation energy of one-valence atoms

In analogy with the expression for second-order correlation energy for closedshell atoms, Eq. (2.41), the second-order correlation energy of one-valence atoms is

$$E^{(2)} = \langle \Phi_v | \overline{V_2 \Omega_2^{(1)}} | \Phi_v \rangle = E^{(2), \text{ core}} + E^{(2), \text{val}}, \qquad (2.44)$$

where $|\Phi_v\rangle$ is the model state function for single-reference atoms. Like in closed-shell case, only closed diagram contribute to $E^{(2)}$. For the core part $E^{(2), \text{ core}}$, diagrams are same as in closed-shell system. However, for the valence part $E^{(2), \text{ val}}$ closed diagrams are those with free valence lines and the diagrams are shown in Fig. 2.4.



Figure 2.4: Diagrams which contribute to second-order correction to the attachment energy.

The experimentally observable quantity is the attachment energy of the valence electron v. It is the energy released when the valence electron is added to the system and is given as

$$E_v^{\text{att}} = \epsilon_v + E^{(2), \text{ val}}.$$
(2.45)

It is equivalent to the calculating ionization potential as the later is negative of the former. Another quantity relevant to experiments are the excitation energies

$$\Delta E = E_v - E_g, \tag{2.46}$$

where E_g is the energy of the ground state function. In the result section the excitation energies for a group of one-valence atoms are presented.

2.4.2 Excitation energy for two-valence atoms

Like in the one-valence system the two-valence many particle states, which belong to the model space, are

$$|\Phi_{vw}\rangle = a_v^{\dagger} a_w^{\dagger} |\Phi_0\rangle, \qquad (2.47)$$

where v and w are valence orbitals. As mentioned earlier, although the many particle states which span the model space are known, the reference states are not defined initially. The reason is the general form of a reference states $|\Phi^{\alpha}\rangle$ is the linear combination

$$|\Phi^{\alpha}\rangle = \sum_{i} c_{i}^{\alpha} |\Phi_{v_{i}w_{i}}\rangle, \qquad (2.48)$$

where c_i^{α} are the coefficients of linear combination. There are no non-trivial way to define these coefficients. The approach is then, perturb first and diagonalize the effective Hamiltonian within the model space. Accordingly, to calculate the second order correlation energy apply the first order wave operator in Eq. (2.33) to all the many particle states $|\Phi_i\rangle \in P$. The next step is then to generate the effective Hamiltonian matrix within the model space with jj coupled states.

2.4.2.1 First- and second-order effective Hamiltonian

Following Eq. (2.36), the first-order correlation energy is

$$H_{\rm eff}^{(1)} = PVP = P(V_0 + V_1 + V_2)P.$$
(2.49)

where, V_0 is the contribution from the close-shell part. This contributes equally to all the states in model space and shifts all the energy levels by the same amount. The one- and two-body terms, V_1 and V_2 , have contributions from open-shell part only. The nonzero contribution in particular from the onebody term adds same to the all diagonal elements of the effective Hamiltonian matrix and is therefore does not account for the energy level splitting. From Eq. (2.49), $H_{\text{eff}}^{(1)}$ is reduced to the form

$$H_{\rm eff}^{(1)} = PV_2P. (2.50)$$

The contributing diagram is a close diagram, shown in Fig. 2.6(a), with a pair of valence lines at each vertex.



Figure 2.5: Representation of the first-order wave operator diagrams for twovalence atoms. Double arrows to the bottom of the interaction represents the valence orbital.

The second-order effective Hamiltonian is

$$H_{\rm eff}^{(2)} = PV\Omega^{(1)}P = P(V_1 + V_2) \left[\Omega_1^{(1)} + \Omega_2^{(1)}\right]P, \qquad (2.51)$$

here, the V_1 contribution is zero when Dirac-Fock orbitals are used in the calculations. The expression of $H_{\text{eff}}^{(2)}$ is then reduced to

$$H_{\rm eff}^{(2)} = P V_2 \Omega_2^{(1)} P.$$
 (2.52)



Figure 2.6: The two-body diagram (a), arises from the first-order effective Hamiltonian $H_{\text{eff}}^{(1)}$. The remaining two-body diagrams, from (b) - (g), contribute to the second-order effective Hamiltonian $H_{\text{eff}}^{(2)}$.

The diagrammatic representation of the first-order wave operator, in Eq. (2.52), is shown in the Fig. 2.5. These contract with the diagrams of V and generates the second order effective Hamiltonian diagrams. These are calculated with respect to uncoupled states and treated as one- and two-body effective operators. The diagrammatic representation of the effective operators are shown in Figs. 2.4 and 2.6.

2.4.2.2 H_{eff} matrix elements with jj coupled states

Electrons being fermions Pauli's exclusion principle must hold true and to preserve this, the many particle wave function of two-valence systems must be antisymmetric. For two non-equivalent electrons, the antisymmetrised jj coupled state may be expressed as

$$|\{\gamma_v j_v m_v \gamma_w j_w m_w\}JM\rangle = \frac{1}{\sqrt{2}} [|(\gamma_v j_v m_v \gamma_w j_w m_w)JM\rangle + (-1)^{j_v + j_w + J} |(\gamma_w j_w m_w \gamma_v j_v m_v)JM\rangle].$$
(2.53)

where, j_v and j_w are the total angular momenta of the single electron states $|\phi_v\rangle$ and $|\phi_w\rangle$ respectively, m_v and m_w are the magnetic quantum numbers, γ_v and γ_w are additional quantum numbers to identify each spin-orbitals uniquely, and J and M are the total angular and magnetic quantum numbers of the coupled state, respectively. Using Eq. (2.53), the matrix element of the Coulomb interaction Hamiltonian is

$$\langle \{j_{x}m_{x}j_{y}m_{y}\}JM|\frac{1}{r_{12}}|\{j_{v}m_{v}j_{w}m_{w}\}JM\rangle = \frac{1}{2} \Big[\\ \langle (j_{x}m_{x}j_{y}m_{y})JM|\frac{1}{r_{12}}|(j_{v}m_{v}j_{w}m_{w})J'M'\rangle - (-1)^{j_{x}+j_{y}-J} \\ \langle (j_{y}m_{y}j_{x}m_{x})JM|\frac{1}{r_{12}}|(j_{v}m_{v}j_{w}m_{w})J'M'\rangle - (-1)^{j_{v}+j_{w}-J'} \\ \langle (j_{x}m_{x}j_{y}m_{y})JM|\frac{1}{r_{12}}|(j_{w}m_{w}j_{v}m_{v})J'M'\rangle + (-1)^{j_{x}+j_{y}+j_{v}+j_{w}-J-J'} \\ \langle (j_{y}m_{y}j_{x}m_{x})JM|\frac{1}{r_{12}}|(j_{w}m_{w}j_{v}m_{v})J'M'\rangle \Big].$$

$$(2.54)$$

While implementing the matrix elements all the four terms in Eq. (2.54) are explicitly calculated with proper normalization factor. To illustrate the procedure consider the direct matrix element in the above equation. In terms of uncoupled states

$$\langle (\gamma_v j_v m_v \gamma_w j_w m_w) JM | \frac{1}{r_{12}} | (\gamma_x j_x m_x \gamma_y j_y m_y) J'M' \rangle = \sum_k (-1)^{j_x + j_w + J + k}$$

$$\delta(J, J') \delta(M, M') \left\{ \begin{array}{cc} j_x & j_x & k \\ j_y & j_w & J \end{array} \right\} \langle \gamma_v j_v \| \mathbf{C}^k \| \gamma_x j_x \rangle \langle \gamma_w j_w \| \mathbf{C}^k \| \gamma_y j_y \rangle R^k.$$
 (2.55)

Where \mathbb{R}^k is the radial integral and \mathbb{C}^k is the spherical tensor operator of rank k. For matrix elements, as evident from the delta functions, to be non-zero the states should have the same parity, J and M. The expression in Eq. (2.55) are applicable to the matrix elements of the two-body diagrams (Fig. 2.6(b-g). In this case the multipole k and the radial integral arise from the combination of two orders of residual Coulomb interactions.

Similarly, the matrix element of the one-body operator of rank k, with respect to the jj coupled states is

$$\langle (\gamma_v j_v \gamma_w j_w) JM | \mathbf{F}^k(1) | (\gamma_x j_x \gamma_y j_y) J'M' \rangle = \delta(\gamma_w, \gamma_y) \delta(j_w, j_y)$$

$$(-1)^{J-M} (-1)^{j_v + j_y + J' + k} [J, J']^{1/2} \begin{pmatrix} J & k & J' \\ -M & 0 & M \end{pmatrix} \begin{cases} j_v & j_x & k \\ J' & J & j_w \end{cases}$$

$$\times \langle \gamma_v j_v \| \mathbf{f}^k \| \gamma_x j_x \rangle.$$

$$(2.56)$$

This is a very general expression and applicable to one-body operator of any rank k. In the present calculations, however, one-body effective operator is scalar (k = 0). Using Eqs. (2.55) and (2.56) the matrix elements of the effective Hamiltonian can be evaluated in the jj coupled states.

2.5 E1PNC from MBPT

In this section we derive the expression for E1PNC transition amplitude using first-order many-body perturbation theory, for one- and two-valence atomic systems. The results obtained from the calculations are discussed in the second last chapter of the thesis.

2.5.1 The one-valence atoms

In the presence of the PNC interaction, the total Hamiltonian of an atom is the sum of the Dirac-Coulomb Hamiltonian and the PNC interaction Hamiltonian. The eigen value equation is modified to

$$(H^{\rm DC} + \lambda H_{\rm PNC}) |\widetilde{\Psi}_i\rangle = (E_i + \lambda E^1) |\widetilde{\Psi}_i\rangle, \qquad (2.57)$$

where $|\widetilde{\Psi}_i\rangle$, is a mixed parity eigen state. It is defined as

$$|\widetilde{\Psi}_i\rangle = |\Psi_i\rangle + \lambda |\overline{\Psi}_i^1\rangle,$$
(2.58)

where $|\overline{\Psi}_i^1\rangle$ is the first-order correction to $|\Psi_i\rangle$. It arises from the H_{PNC} induced mixing from opposite parity state.

In MBPT, the wave functions $|\Psi_v\rangle$ and $|\bar{\Psi}_v^1\rangle$ are evaluated using the expressions

$$|\Psi_v\rangle \approx (1+\Omega^{(1)})|\Phi_v\rangle, \text{ and } |\bar{\Psi}_v^1\rangle = \Omega_{\text{PNC}}^{(1)}|\bar{\Psi}_v\rangle.$$
 (2.59)

To avoid the complexity of the equations restrict to the first-order correction only. It is, however, possible to extend the method up to second-order without much difficulty. But going beyond the second order requires a very systematic approach and huge computational resources. The wave operator Ω , as describe in the previous sections, incorporates the correlation effects. And the wave operator Ω_{PNC} incorporates the effects of PNC interaction. Using (2.59), the PNC induced electric dipole transition amplitude is

$$E1PNC = \langle \Phi_w \| \left(1 + \Omega^{(1)} + \lambda \Omega^{(1)}_{PNC} \right)^{\dagger} \mathbf{D} \left(1 + \Omega^{(1)} + \lambda \Omega^{(1)}_{PNC} \right) \| \Phi_v \rangle.$$
(2.60)

Retaining only the terms which are first order in the perturbation parameter λ

E1PNC =
$$\langle \Phi_w \| (1 + \Omega^{(1)})^{\dagger} \boldsymbol{D} \Omega_{PNC}^{(1)} + \Omega_{PNC}^{(1)}^{\dagger} \boldsymbol{D} (1 + \Omega^{(1)}) \| \Phi_v \rangle,$$

= $\langle \Phi_w \| \boldsymbol{D} \Omega_{PNC}^{(1)} + \Omega_{PNC}^{(1)}^{\dagger} \boldsymbol{D} + \Omega^{(1)\dagger} \boldsymbol{D} \Omega_{PNC}^{(1)} + \Omega_{PNC}^{(1)}^{\dagger} \boldsymbol{D} \Omega^{(1)} \| \Phi_v \rangle.$ (2.61)

This is the expression for one-valence systems and can be extended to the two-valence systems. The corresponding diagrams of the first and third terms in Eq. (2.61) are are shown in the Fig. 2.7. The diagrams arising from the second and fourth terms are obtained by taking the Hermitian conjugate of those from first and third terms, respectively.

2.5.2 The two-valence atoms

The PNC perturbed atomic state function using first-order MBPT, for two-valence atoms is

$$|\tilde{\Psi}_i\rangle = \left(1 + \Omega^{(1)} + \lambda \Omega^{(1)}_{\text{PNC}}\right) \sum_k c_k^i |\Phi_k\rangle, \qquad (2.62)$$

where $\Omega^{(1)}$ and $\Omega^{(1)}_{PNC}$, as mentioned in the previous section, are the wave operators corresponding to the residual Coulomb and the PNC interactions respectively. c_k^i is the expansion coefficient, when a two-valence exact wave function is expanded in terms of the configuration state functions contributing



Figure 2.7: Diagrams which contribute to the first (diagrams (m) and (n)) and third (remaining diagrams) terms of the Eq. (2.61). The dashed line represents the residual perturbation and the solid line ended with the circle is to represent the dipole operator. The solid line having square at the end represents the PNC operator.

to the model space. And $|\Phi_k\rangle$ is the two-valence configuration included in the model space. Using Eq. (2.62) and following the similar steps as the one-valence case, we get

$$E1PNC = \sum_{j,k} c_j^{f^*} c_k^i \langle \Phi_j \| \mathbf{D}\Omega_{PNC}^{(1)} + \Omega_{PNC}^{(1)} \mathbf{D} + \Omega_{PNC}^{(1)} \mathbf{D}\Omega_{PNC}^{(1)} + \Omega_{PNC}^{(1)} \mathbf{D}\Omega^{(1)} \| \Phi_k \rangle 2.63)$$

This is the first-order MBPT expression of E1PNC for two-valence atoms. As evident, it requires an additional task of calculating the coefficients $c_i^{f^*}$ and c_k^i .

The diagrammatic evaluation of the Eq. (2.63) consist of the diagrams which have two pairs of free lines as the valence. The terms first and second contribute through one spectator valence line. The contributing diagrams to the terms fist and third are shown in the Fig. 2.8. The diagrams which contribute to second and fourth terms are not given, as the terms second and fourth are the Hermitian conjugate of first and third respectively. These are however included in the actual calculations.



Figure 2.8: Diagrams which contribute to the first (diagrams (a) and (b)) and third (diagrams from (c) to (l)) terms of the Eq. (2.63). The Hermitian conjugate diagrams are not shown.

2.6 Summary of the results

2.6.1 Basis functions

The first step and perhaps the most important in precision atomic calculations is the generation of good quality orbitals. The results described and discussed are from computations with Gaussian type orbitals (GTOs), optimized to reproduce the numerical single particle energies and self consistent field (SCF) energy. The GTOs are even tempered, which unlike the universal basis, the exponent parameters α_0 and β are different for each symmetries. This provides more flexibility to obtained a good quality basis. The numerical results are obtained using the multi-configuration Dirac-Fock code GRASP92 [54]. The exponent parameters of the inert gas atoms and alkaline-Earth ions are listed in Tables. 2.1 and 2.2, respectively. To start with we use the parameters of Tatewaki and collaborators [55] and then optimize further.

2.6.2 Correlation energy of closed-shell atoms

The ground state SCF energy ($E_{\rm DC}^{(0)}$), the second order correlation energy ($E_{\rm corr}^{(2)}$), and the total energy (E) of the inert gas atoms are listed in Table. 2.3. For comparison, the results from previous calculations are also listed in the table. The results from Ishikawa and collaborators [56], the only previous work which incorporate relativistic effects, is chosen for a detailed comparison with the results from the present studies. The SCF energy from the present work, for all the atoms, are slightly lower than the results in Ishikawa's et al [56]. And as noticeable in Table. 2.3, the correlation energies from the present work are, except for Xe, slightly higher. Consequently, the total energy (E) are in good agreement with the values of Ishikawa et al.

Atom	Symmetry	α_0	β	Basis function
²⁰ Ne	s	0.0925	1.4500	38
	p	0.1951	2.7103	35
	d	0.0070	2.7000	25
$^{40}\mathrm{Ar}$	s	0.0985	1.8900	38
	p	0.0072	2.9650	35
	d	0.0070	2.7000	28
$^{84}\mathrm{Kr}$	s	0.0002	2.0220	30
	p	0.0072	2.3650	28
	d	0.0070	2.5500	25
$^{132}\mathrm{Xe}$	s	0.0001	2.0220	32
	p	0.0072	2.3650	28
	d	0.0070	2.5500	25

Table 2.1: Basis set of the parameters, α_0 and β , used in the correlation energy calculations for inert gas atoms.

To investigate the electron correlation effects in more detail, $E_{\rm corr}^{(2)}$ is calculated with systematic inclusion of higher symmetry orbitals-higher orbital angular momentum l-in a sequence. The cumulative contributions from various symmetries to $E_{\rm corr}^{(2)}$ are presented in the Table. 2.4. The value of Ne ground state correlation energy -0.3811, computed with orbitals up to *i* symmetry is in very good agreement with the value -0.3836 from a similar calculations of Lindgren and collaborators [57]. The difference between the two results is at the millihartree level. In this analysis, it is observed that contributions from the higher l orbitals to $E_{\rm corr}^{(2)}$ is negligible for lighter atoms. For heavier atoms, however, a systematic inclusion of higher l orbitals can improve the results. The contribution from k (l = 9) symmetry to $E_{\text{corr}}^{(2)}$ of Ne is -0.0007 and in percentage it is 0.20%. It is however, 0.24%, 0.45% and 0.59% for Ar, Kr and Xe, respectively. The Fig. 2.9 shows the variation of change in $E_{\rm corr}^{(2)}$ when the orbitals from higher symmetries are included in the virtual space. It is evident that, the pattern of the largest contribution are from the p, d, d and f symmetries for Ne, Ar, Kr and Xe, respectively. On further examination, the most dominant contributions are from the core-core combinations of $2p_{3/2}2p_{3/2}$, $3p_{3/2}3p_{3/2}$, $3d_{5/2}3d_{5/2}$ and $4d_{5/2}4d_{5/2}$ for Ne, Ar, Kr and Xe respectively. The variation of cumulative correlation energy with the orbitals is shown in the Fig. 2.10.

Ion	Symmetry	α_0	β	Basis function
$^{25}\mathrm{Mg^{+}}$	s	0.0083	2.8900	28
	p	0.0072	2.9650	25
	d	0.0070	2.7200	22
$^{43}\mathrm{Ca}^+$	s	0.0063	2.8800	29
	p	0.0072	2.9650	26
	d	0.0070	2.7000	24
$^{87}\mathrm{Sr}^+$	s	0.0083	2.9800	30
	p	0.0072	2.9650	27
	d	0.0070	2.8000	25
$^{137}\mathrm{Ba^{+}}$	s	0.0063	2.9800	31
	p	0.0072	2.9590	28
	d	0.0070	2.4500	26

Table 2.2: Basis set parameters, α_0 and β , used in the excitation energy calculations for alkaline Earth ions.

2.6.3 Excitation energy of one-valence atoms

To examine the MBPT for one-valence systems, the attachment energies of $S_{1/2}$ (ground state), and first excited $P_{1/2}$, $P_{3/2}$, $D_{3/2}$ and $D_{5/2}$ states of Mg⁺, Ca^+ , Sr^+ , and Ba^+ ions are calculated from Eq. (4.35). From these using Eq. (2.46), the excitation energies are also evaluated. The results from these calculations are listed in the Table. 2.5. Like in previous case-closed-shell correlation energy-results from the previous theoretical works and experimental are listed for comparison. Among the previous works, Guet and collaborators [65] employed the same many-body method as ours but used a different basis, namely B-spline functions. For most of the states the differences between the current results, and Guet and collaborators [65] is at the millihartree level. More importantly, the difference is random in nature. The deviations may be attributed to the nature of the basis functions used in the two calculations. As evident from Table. 2.5, in the case of Mg⁺ the excitation energies of states $3d \ ^2D_{3/2,5/2}$ are higher than that of $3p \ ^2P_{1/2,3/2}$ states. The sequence is, however, reversed for other ions. This is consistent with the theoretical [65] results and experiment data.

Deviations from the experimental data gradually increases from Mg⁺ to Ba⁺. The excitation energies of the $P_{1/2}$, $P_{3/2}$, $D_{3/2}$ and $D_{5/2}$ states of Mg⁺ differ form the experiment by 0.11%, 0.10%, 0.21% and 0.21% respectively. In the case of Ba⁺, these are however 4.12%, 4.13%, 9.91% and 6.23% for $P_{1/2}$, $P_{3/2}$, $D_{3/2}$ and $D_{5/2}$ states, respectively. Another important observation is, except for Sr⁺, large is deviation is observed in the $D_{3/2}$ and $D_{5/2}$ excitation energies for all the ions. However for Sr⁺ the excitation energies of $P_{1/2}$ and

Table 2.3: The SCF $E_{DC}^{(0)}$, the second-order correlation $E_{corr}^{(2)}$, and the total energies E of Ne, Ar, Kr and Xe atomic systems. All the values listed are in atomic units. For comparison results from other calculations are also listed.

Ā	Atom		This work		Other	work
		$E_{DC}^{(0)}$	$E_{\rm corr}^{(2)}$	E	$E_{DC}^{(0)}$	$E_{\rm corr}^{(2)}$
	²⁰ Ne	-128.6932	-0.3830	-129.0762	-128.6919	$-0.3834^{\rm a}$
						-0.3836^{b}
						-0.3822^{c}
						$-0.3697^{\rm d}$
						$-0.3804^{\rm e}$
	$^{40}\mathrm{Ar}$	-528.6882	-0.6938	-529.3820	-528.6838	$-0.6981^{\rm a}$
						$-0.6822^{\rm e}$
						$-0.685^{\rm f}$
						-0.790^{g}
;	84 Kr	-2788.8659	-1.8426	-2790.7085	-2788.8615	$-1.8468^{\rm a}$
1	$^{132}\mathrm{Xe}$	-7446.8887	-2.9767	-7449.8654	-7446.8880	$-2.9587^{\rm a}$
^a Refe ^d Refe ^g Refe	erence erence erence	[56]. ^b Refe [60]. ^e Refe [58].	rence[57]. rence[61].	^c Reference ^f Reference	[59]. [62].	

Table 2.4: Cumulative second-order correlation energy, calculated using MBPT, when orbitals up to k symmetry are included in the virtual space. All values are in atomic units.

Symmetry	Ne	Ar	Kr	Xe
s	-0.0194	-0.0210	-0.0236	-0.0247
p	-0.1920	-0.2043	-0.2479	-0.2687
d	-0.3216	-0.5401	-0.9512	-1.0419
f	-0.3589	-0.6330	-1.5213	-2.2972
g	-0.3732	-0.6695	-1.7077	-2.6879
h	-0.3786	-0.6830	-1.7843	-2.8520
i	-0.3811	-0.6891	-1.8179	-2.9238
j	-0.3823	-0.6921	-1.8343	-2.9591
k	-0.3830	-0.6938	-1.8426	-2.9767

Table 2.5: Ionization potential and excitation energies calculated using MBPT. For comparison other results and experimental values are also listed. All values are in atomic units.

Ion	state	This v	work	Other	works	Exp.Ref[63].
		IP	EE	IP	EE	EE
$^{25}\mathrm{Mg^{+}}$	$3s_{1/2}$	-0.55156	0.0	-0.55252	0.0	0.0
	$3d_{3/2}$	-0.22652	0.32504	-0.22677	$0.32575^{\rm a}$	0.32573
	$3d_{5/2}$	-0.22652	0.32504	-0.22677	0.32575^{a}	0.32574
	$3p_{1/2}$	-0.38922	0.16234	-0.39003	0.16249^{a}	0.16252
	$3p_{3/2}$	-0.38878	0.16278	-0.38961	$0.16291^{\rm a}$	0.16294
$^{43}\mathrm{Ca}^+$	$4s_{1/2}$	-0.43784	0.0	-0.43836	0.0	0.0
	$3d_{3/2}$	-0.37797	0.05987	-0.37768	$0.06068^{\rm b}$	0.06220
	$3d_{5/2}$	-0.37762	0.06022	-0.37731	$0.06205^{\rm b}$	0.06247
	$4p_{1/2}$	-0.32180	0.11604	-0.32217	$0.11619^{\rm b}$	0.11478
	$4p_{3/2}$	-0.32075	0.11709	-0.32111	0.11725^{b}	0.11580
$^{87}\mathrm{Sr^{+}}$	$5s_{1/2}$	-0.40788	0.0	-0.40839	0.0	0.0
	$4d_{3/2}$	-0.34236	0.06552	-0.34279	$0.06560^{\rm b}$	0.06632
	$4d_{5/2}$	-0.34091	0.06697	-0.34132	$0.06707^{\rm b}$	0.06760
	$5p_{1/2}$	-0.29793	0.10995	-0.29838	0.11001^{b}	0.10805
	$5p_{3/2}$	-0.29421	0.11367	-0.29463	0.11376^{b}	0.11171
$^{137}\text{Ba}^{+}$	$6s_{1/2}$	-0.37297	0.0	-0.37308	0.0	0.0
	$5d_{3/2}$	-0.35296	0.02001	-0.35172	0.02136^{b}	0.02221
	$5d_{5/2}$	-0.34872	0.02425	-0.34748	0.02560^{b}	0.02586
	$6p_{1/2}$	-0.27685	0.09612	-0.27532	0.09776^{b}	0.09232
	$6p_{3/2}$	-0.26882	0.10415	-0.26946	0.10362^{b}	0.10002

^a Reference[64]. ^b Reference[65].



Figure 2.9: Diagram showing the change in the second-order correlation energy with the various symmetries.



Figure 2.10: Diagram showing the cumulative second-order correlation energy when orbitals from higher symmetries are included.

 $P_{3/2}$ are larger and it is not the $D_{3/2}$ and $D_{5/2}$ states as in other ions.

2.6.4 Excitation energy for two-valence atoms

In this section we examine the two-electron removal and the excitation energies calculated using MBPT for two-valence atoms. For this, we choose Mg, Ca, Sr, Ba, and Yb atomic systems. Except Ca and Sr, all the other atoms have different energy level sequence, and therefore would be a good test for the reliability of the method. In all the cases we calculate the ground state and eight exited states. In these calculations we have used Vn - 2 single-electron orbitals.

In Table. 2.6 we present the excitation energies for atomic Mg. The fine

Table 2.6: Two-electron removal and excitation energies for ground and some of the low lying excited states of Mg and Ca, calculated using MBPT. All values are in atomic units.

State	($\operatorname{Exp.Ref}[63].$	
	E_{vw}	EE	EE
		$^{26}Mg; [Ne]3s^2$	
$3s^{2} {}^{1}S_{0}$	-0.80564	0.0	0.0
$3s3p \ ^{3}P_{0}$	-0.71417	0.09147	0.09956
$3s3p \ ^{3}P_{1}$	-0.71422	0.09142	0.09965
$3s3p \ {}^{3}P_{2}$	-0.71433	0.09131	0.09983
$3s3p \ ^{1}P_{1}$	-0.62485	0.18079	0.15971
$3s3d \ ^{1}D_{2}$	-0.59869	0.20695	0.21143
$3s3d \ ^{3}D_{2}$	-0.57183	0.23381	0.21851
$3s3d \ ^{3}D_{3}$	-0.57183	0.23381	0.21851
$3s3d \ ^{3}D_{1}$	-0.57183	0.23381	0.21851
		40 0	
		${}^{40}\text{Ca}; [\text{Ar}]4s^2$	
$4s^{2} {}^{1}S_{0}$	-0.63336	0.0	0.0
$4s4p \ {}^{3}P_{0}$	-0.56980	0.06356	0.06906
$4s4p \ {}^{3}P_{1}$	-0.56995	0.06341	0.06930
$4s4p \ {}^{3}P_{2}$	-0.57026	0.06310	0.06978
$4s3d \ ^{3}D_{1}$	-0.51987	0.11349	0.09265
$4s3d \ ^{3}D_{2}$	-0.52000	0.11336	0.09272
$4s3d \ ^{3}D_{3}$	-0.52016	0.11320	0.09282
$4s3d \ ^{1}D_{2}$	-0.51314	0.12022	0.09955
$4s4p \ ^{1}P_{1}$	-0.51722	0.11614	0.10777

structure splitting of the configuration 3s3d is found to be consistent with the experimental data. This is however not correct for the configuration 3s3p. ${}^{3}P_{2}$ appears first then ${}^{3}P_{1}$ followed by ${}^{3}P_{0}$. The two-electron removal energy of our result is about 3.3% smaller than the experiment. The discrepancy in excitation energy is observed to be larger than the case of Mg⁺. The error in the ${}^{3}P_{J}$ states is approximately about 8.5%. This is however significantly large, about 13.2%, in the case of ${}^{1}P_{1}$. Unlike ${}^{1}P_{1}$, the state ${}^{1}D_{2}$ is closer to the experiment. The deviations are about 2.1% and 7.0% respectively for the states ${}^{1}D_{2}$ and ${}^{3}D_{J}$.

The ground state energy of Ca, like the Mg, is smaller than the experiment. The difference is 4.2%, slightly larger than the Mg. Fine structure splittings for both the configurations, 4s4p and 3d4s, are different than the experiment. Like Mg, ${}^{3}P_{2}$ appears first then ${}^{3}P_{1}$ followed by ${}^{3}P_{0}$. The same sequence is observed for ${}^{3}D_{J}$ states also. As its evident from Table. 2.6, the excitation energies of ${}^{3}P_{J}$ states are lower than the experimental results. It is however higher in the case of ${}^{1}P_{1}$. The deviations for the states ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}P_{2}$ and ${}^{1}P_{1}$ are 8.0%, 8.4%, 9.6% and 7.8% respectively. In contrary to the ${}^{3}P_{J}$ states, the excitation energies for ${}^{3}D_{J}$ and ${}^{1}D_{2}$ are greater than the experimental values. In this case discrepancy is even larger, about 22% and 20.8% respectively for ${}^{3}D_{J}$ and ${}^{1}D_{2}$, in comparison to the triplet and singlet P.

As we see in the Table. 2.7, the atomic Sr follow the same energy levels sequence as Ca. We find, for this atom our computed sequence of the states is in agreement with the experiment. Like Mg and Ca, the two-electron excitation energy, -0.58512, of our results is smaller, by 4.8%, than that of the experiment. The excitation energies for all the states follow the same pattern as in the case of Ca. These are lowered by 0.5%, 10.9% and 11.9% respectively for ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{3}P_{2}$ states, than the experimental values. The excitation energies are however higher for the states ${}^{1}P_{1}$, ${}^{3}D_{J}$, and ${}^{1}D_{2}$. The differences are 28%, $\approx 14\%$ and 13.4% respectively.

The atomic Ba shows different energy level structure than the atomic Mg, Ca and Sr. Unlike the Mg, Ca and Sr, the states of the configuration 5d6s appear lower to that of the 6s6p. The results from our calculations are listed in the Table. 2.7. Our calculated energy levels sequence differ than the experiment. Like the other atoms, the ground state energy is lower than the experiment. The discrepancy is slightly larger, it is about 5%, than the Mg, Ca, and Sr. The excitation energies for the triplet and singlet D are greater than the experiment. These are however smaller for the triplet and singlet P. Errors with respect to the experimental results have further increased in comparison to Mg, Ca, and Sr. These are 24.6%, 23.3%, 20.3% and 22.2% respectively for the states ${}^{3}D_{1}$, ${}^{3}D_{2}$, ${}^{3}D_{3}$ and ${}^{1}D_{2}$. The less deviations, 10.5%, 10.8%, 12% and 0.2% respectively, are observed for ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}P_{2}$ and ${}^{1}P_{1}$ states.

The parameters α_0 and β used to optimize the basis for Yb are given in

Table 2.7: Two-electron removal and excitation energies for ground and some of the low lying excited states of Sr and Ba, calculated using MBPT. All values are in atomic units.

State	(Durs	Exp.Ref[63].
	E_{vw}	\mathbf{EE}	EE
		87 Sr; [Kr] $5s^2$	
$5s^{2} {}^{1}S_{0}$	-0.58512	0.0	0.0
$5s5p \ {}^{3}P_{0}$	-0.52673	0.05839	0.06524
$5s5p \ {}^{3}P_{1}$	-0.52627	0.05885	0.06609
$5s5p \ {}^{3}P_{2}$	-0.52534	0.05978	0.06788
$5s4d \ ^{3}D_{1}$	-0.49050	0.09462	0.08274
$5s4d \ {}^{3}D_{2}$	-0.49046	0.09466	0.08301
$5s4d \ ^{3}D_{3}$	-0.49038	0.09474	0.08347
$5s4d \ ^{1}D_{2}$	-0.48105	0.10407	0.09181
$5s4d \ ^{1}P_{1}$	-0.48347	0.10165	0.09887
		137 Ba; [Xe]6 s^2	
$6s^{2} {}^{1}S_{0}$	-0.53110	0.0	0.0
$6s5d \ ^{3}D_{1}$	-0.47983	0.05127	0.04116
$6s5d \ ^{3}D_{2}$	-0.47934	0.05176	0.04199
$6s5d \ ^{3}D_{3}$	-0.47847	0.05263	0.04375
$6s5d \ ^{1}D_{2}$	-0.46768	0.06342	0.05192
$6s6p \ {}^{3}P_{0}$	-0.48108	0.05002	0.05589
$6s6p \ {}^{3}P_{1}$	-0.47976	0.05134	0.05758
$6s6p \ {}^{3}P_{2}$	-0.47691	0.05419	0.06158
$6s6p \ ^{1}P_{1}$	-0.44901	0.08209	0.08229

Table 2.8: Basis set parameters, α_0 and β , used in the excitation energy calculations for atomic Yb.

Symmetry	α_0	β	Basis function
s	0.0077	2.8400	36
p	0.0075	2.8420	33
d	0.0072	2.670	31
f	0.0071	2.701	29

State		Exp.Ref[63].	
	E_{vw}	EE	EE
		173 Yb; [Xe] $4f^{14}6s^2$	
$6s^{2} {}^{1}S_{0}$	-0.63659	0.0	0.0
$6s6p \ {}^{3}P_{0}$	-0.56743	0.06916	0.07877
$6s6p \ {}^{3}P_{1}$	-0.56454	0.07205	0.08198
$6s6p \ {}^{3}P_{2}$	-0.55814	0.07845	0.08981
$6s5d \ ^{3}D_{1}$	-0.51488	0.12171	0.11158
$6s5d \ ^{3}D_{2}$	-0.51394	0.12265	0.11278
$6s6p \ ^{1}P_{1}$	-0.51671	0.11988	0.11422
$6s5d \ ^{3}D_{3}$	-0.51216	0.12443	0.11514
$6s5d \ ^{1}D_{2}$	-0.50034	0.13625	0.12611

Table 2.9: Two-electron removal and the excitation energies for states of Yb calculated using MBPT. All values are in atomic units.

the Table. 2.8. The excitation energies are presented in the Table. 2.9. As its apparent from the Table. 2.9, energy levels of this atom show even complicated pattern than the previously described atoms. It is ${}^{1}P_{1}$, lies between ${}^{3}D_{2}$ and ${}^{3}D_{3}$, which differentiate from Ca and Sr atoms. In the present theoretical study, ${}^{1}P_{1}$ is situated above the ${}^{3}P_{2}$. Like Ca, Sr, and Ba, the excitation energy of triplet P is less, and same for the triplet D is greater, than the experimental results. The largest discrepancy is observed in ${}^{3}P_{J}$ state, and it is approximately 12.5%. This is less than 13.2% for ${}^{1}P_{1}$ in Mg, 22% for ${}^{3}D_{J}$ in Ca, 28% for ${}^{1}P_{1}$ in Sr, and 24% for ${}^{3}D_{1}$ in Ba, implying different nature of the electron correlation in Yb. This is ascribed to the fact that unlike the other atoms considered, Yb has 4f electrons.

The large discrepancy in the excitation energy, in all the atoms, is attributed partly to the nature of the method, as electron correlation is considered only up to the second-order perturbation, and partly to the nature of the potential we choose.

Chapter 3

Perturbed configuration interaction

For quantum systems the wave function and energy are the basic ingredients to describe it's properties. These are obtained, in general, by solving the Schroedinger equation and in the case of atoms it is

$$H_a|\Psi\rangle = E|\Psi\rangle,\tag{3.1}$$

where H_a is the atomic Hamiltonian, E and $|\Psi\rangle$ are the energy and the wave function respectively. Solving the above equation for many-electron atoms/ions, is however, not possible due to the electron-electron interaction. With Hartree-Fock theory [47], the solution is separated into mean field and perturbative parts. It is an ideal starting point to calculate approximate singleelectron wave functions and the energies. However, it does not take into account for the electron-electron repulsion term.

Configuration Interaction [50, 66], best suited for small systems [67], is a post Dirac-Fock theory. It diagonalizes the Hamiltonian matrix in a many particle basis to account for the electron correlation effects in the atoms/ions. Properties calculations, especially in case E1PNC calculation, using CI wave functions requires diagonalization of two sets of matrices: one each in the two opposite parity subspaces. This is computationally expensive both in memory and operations. The is problem is partly mitigated in the Perturbed CI theory. In this theory, there is only one diagonalization and the second diagonalization is recast as solving a set of linear algebraic equations.

This chapter is organized as follows: Section. I describes the CI method, and PCI is discussed in Section. II of the chapter. Application to the atomic Yb is described in Section. III. And results hence obtained are presented in the last section of the chapter.

3.1 Configuration interaction

The Configuration interaction (CI) is a *variational* based method and widely used in atomic and molecular physics calculations. The exact wave function in CI theory [50, 66] is defined as

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ap} c_a^p |\Phi_a^p\rangle + \frac{1}{(2!)^2} \sum_{abpq} c_{ab}^{pq} |\Phi_{ab}^{pq}\rangle + \frac{1}{(2!)^2} \sum_{abcpqr} c_{abc}^{pqr} |\Phi_{abc}^{pqr}\rangle + \cdots \quad (3.2)$$

where, indices $a, b, c, \dots (p, q, r, \dots)$ represent the occupied (virtual) orbitals. In terms of CSFs, $|\Phi_0\rangle$ is the dominant or the reference state of $|\Psi\rangle$, $|\Phi_a^p\rangle$ is a singly excited CSF, where an electron from occupied orbital a is excited to the virtual orbital p. Similarly, $|\Phi_{ab}^{pq}\rangle$ is a doubly excited CSF and so on till all the electrons in the occupied shells are excited to virtual shells. The multiplying factors $1/(n!)^2$ ensures no double counting occurs and c_{\dots}^{\dots} are the mixing coefficients. The mixing coefficients are such that the wave function is normalized

$$\langle \Psi | \Psi \rangle = \sum_{ij} c_i c_j \langle \Phi | \Phi \rangle = \sum_i c_i^2 = 1, \qquad (3.3)$$

for convenience of notation c_{i} are shortened to c_i . To calculate c_i define the energy functional

$$\mathcal{E} = \langle \Psi | H | \Psi \rangle - \lambda (\langle \Phi | H | \Phi \rangle - 1) = \sum_{ij} c_i c_j \langle \Phi_i | H | \Phi_j \rangle - \lambda (\langle \Phi | H | \Phi \rangle - 1).$$
(3.4)

Here λ is a Langrange undetermined multiplier to incorporate the normalization condition as a constraint. The mixing coefficients are solution of the variational minimization

$$\delta \mathcal{E} = 0, \tag{3.5}$$

with c_i as parameters of variation. This leads to an eigenvalue equation and for a CI calculation with n CSFs, the eigenvalue equation is

$$\sum_{j} H_{ij} c_j = \lambda c_i, \qquad i = 0, 2, \cdots, n - 1.$$
(3.6)

In matrix notation

$$Hc = Ec. (3.7)$$

This is the standard eigen value equation. And in actual implementation, CI calculation amounts to diagonalization of the Hamiltonian matrix. The lowest eigen value is an upper bound to the ground state energy. And in the same way, higher eigen values are upper bound to the excited states of the atom.

3.1.1 Single-double CI

The CI method, in principle, provides an exact solution of the many-electron Schroedinger equation. However, in practice, it is computationally impossible to implement for atoms or ions with a large number of electrons as the number of CSFs increases exponentially with the number of electrons. This follows from the ${}^{M}C_{N}$ scaling of arranging N electrons in M orbitals, where in general $M \gg N$. Even for small atom or molecules with moderate size basis sets, the full CI matrix can be as large as $10^{9} \times 10^{9}$. One simple way to reduce the size of the matrix is truncate the full CI expansion in Eq. (3.2). A reasonable truncation, which captures correlation effects quite accurately, is the singledouble approximation. Where CSFs up to double excitation are retained, the CI wave function is then

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ap} c_a^p |\Phi_a^p\rangle + \frac{1}{(2!)^2} \sum_{abpq} c_{ab}^{pq} |\Phi_{ab}^{pq}\rangle.$$
(3.8)

The contribution from the singly excited states to the correlation energy is negligibly small compared to the double excitation. However, these can can be included in the CI expansion without complicating the expression as singles are much less in number than the doubles. The Hamiltonian matrix is then

$$\begin{bmatrix} \langle \Phi_0 | H | \Phi_0 \rangle & 0 & \langle \Phi_0 | H | \Phi_{ab}^{pq} \rangle \\ 0 & \langle \Phi_a^p | H | \Phi_a^p \rangle & \langle \Phi_a^p | H | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | H | \Phi_0 \rangle & \langle \Phi_{ab}^{pq} | H | \Phi_a^p \rangle & \langle \Phi_{ab}^{pq} | H | \Phi_{ab}^{pq} \rangle \end{bmatrix}.$$
(3.9)

This is the CI matrix within the single-double approximation and c_0 , c_a^p , and c_{ab}^{pq} are obtained by diagonalizing it. From the above matrix elements we can make two important observations. First, $\langle \Phi_0 | H | \phi_a^p \rangle = 0$ this implies that the single excitations do not coupled with the reference state. Which is a consequence of the Brillouin's theorem. And second, doubly excited states mixes with the reference state and accounts for the correlations effects.

3.1.2 E1PNC matrix element using CI

$$\boldsymbol{D} = q\boldsymbol{r},\tag{3.10}$$

where q is the electric charge and r is the position vector of the particle considered. Since in our case the charge particle is an electron, the above equation can further be written as

$$\boldsymbol{D} = -e\boldsymbol{r},\tag{3.11}$$

where e is the electric charge of the electron and in atomic unit it is equal to one.

In the presence of parity violating interaction Hamiltonian $H_{\rm PNC}$, which arise from the weak interactions or other interactions which are beyond the standard model of particle physics, the atomic Hamiltonian is then modified to

$$H_{a} = H^{DC} + \lambda H_{PNC},$$

$$= \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_{i} \cdot \boldsymbol{p}_{i} + (\beta - 1)c^{2} - \frac{Z}{r_{i}} \right] + \sum_{i < j} \frac{1}{r_{ij}} + \lambda H_{PNC}.$$
 (3.12)

Here, λ is the perturbation parameter. The atomic Hamiltonian satisfy the eigenvalue equation

$$(H^{\rm DC} + \lambda H_{\rm PNC}) |\widetilde{\Psi}_i\rangle = (E_i + \lambda E^1) |\widetilde{\Psi}_i\rangle, \qquad (3.13)$$

where $|\widetilde{\Psi}_i\rangle$, is a mixed parity eigen state. It is defined as

$$|\widetilde{\Psi}_i\rangle = |\Psi_i\rangle + \lambda |\overline{\Psi}_i^1\rangle, \qquad (3.14)$$

where $|\overline{\Psi}_i^1\rangle$ is the first-order correction to $|\Psi_i\rangle$. It arises from the H_{PNC} induced mixing from opposite parity state. Due to the parity mixing, two states of same parity $|\Psi_i\rangle$ and $|\Psi_f\rangle$ acquires a finite dipole transition amplitude

E1PNC =
$$\langle \widetilde{\Psi}_f | \boldsymbol{D} | \widetilde{\Psi}_i \rangle = \left[\langle \Psi_f | + \lambda \langle \overline{\Psi}_f^1 | \right] \boldsymbol{D} \left[| \Psi_i \rangle + \lambda | \overline{\Psi}_i^1 \rangle \right].$$
 (3.15)

Considering that $\langle \Psi_f | \boldsymbol{D} | \Psi_i \rangle = 0$, and λ is a small parameter, we can retain only those terms which are linear in λ . Dropping the perturbation parameter

E1PNC =
$$\langle \Psi_f | \boldsymbol{D} | \overline{\Psi}_i^1 \rangle + \langle \overline{\Psi}_f^1 | \boldsymbol{D} | \Psi_i \rangle.$$
 (3.16)

Using time independent perturbation theory, the first-order correction to wave function is

$$|\overline{\Psi}_{i}^{1}\rangle = \sum_{I} \frac{\langle \overline{\Psi}_{I} | H_{\text{PNC}} | \Psi_{i} \rangle}{E_{i} - E_{I}} | \overline{\Psi}_{I} \rangle.$$
(3.17)

 $|\overline{\Psi}_I\rangle$ is an intermediate exact atomic eigen state obtained from diagonalizing the CI matrix in the opposite parity space. Using this expression, Eq. (7.3) assumes the form

$$E1PNC = \sum_{I} \left[\frac{\langle \Psi_{f} | \boldsymbol{D} | \overline{\Psi}_{I} \rangle \langle \overline{\Psi}_{I} | H_{PNC} | \Psi_{i} \rangle}{E_{i} - E_{I}} + \frac{\langle \Psi_{f} | H_{PNC} | \overline{\Psi}_{I} \rangle \langle \overline{\Psi}_{I} | \boldsymbol{D} | \Psi_{i} \rangle}{E_{f} - E_{I}} \right].$$
(3.18)

Putting the expression of ASFs, Eq. (2.19), as linear combination of CSFs, we can further write

$$E1PNC = \sum_{I} \sum_{kjlm} a_{k}^{*f} a_{j}^{I} a_{l}^{*I} a_{m}^{i} \left[\frac{\langle \Phi_{k} | \vec{D} | \overline{\Phi}_{j} \rangle \langle \overline{\Phi}_{l} | H_{PNC} | \Phi_{m} \rangle}{E_{i} - E_{I}} + \frac{\langle \Phi_{k} | H_{PNC} | \overline{\Phi}_{j} \rangle \langle \overline{\Phi}_{l} | \vec{D} | \Phi_{m} \rangle}{E_{f} - E_{I}} \right]$$
(3.19)

This is the expression of E1PNC derived using the wave functions calculated in CI theory. As its clear from Eq. (7.4), this approach requires two diagonalizations, one each in the two opposite parity CSF subspaces. When the number of CSFs are large, the diagonalization approach is less desirable in terms of computational efficiency and memory requirement. In the next section we show that the problem of occurrence diagonalization of the CI matrix in two opposite parity subspaces can be mitigated using Perturbed configuration interaction method.

3.2 Perturbed CI equations

The H_{PNC} perturbed eigen state, given in Eq. (2.19), can be written in terms of CSFs as

$$\begin{aligned} |\widetilde{\Psi}_{i}\rangle &= \sum_{k} a_{k}^{i} |\Phi_{k}\rangle + \lambda \sum_{j} c_{j}^{i} \sum_{k} a_{k}^{j} |\overline{\Phi}_{k}\rangle, \\ &= \sum_{k} a_{k}^{i} |\Phi_{k}\rangle + \lambda \sum_{k} d_{k}^{i} |\overline{\Phi}_{k}\rangle. \end{aligned} (3.20)$$

Here, we have used $|\Psi_i\rangle = \sum_k a_k^i |\Phi_k\rangle$ and $\sum_j c_j^i \sum_k a_k^j = \sum_k d_k^i$, where the coefficients c_j^i and a_k^j are combined with respect to the dummy index j to give a single coefficients d_k^i . This coefficient subsumes or combines the effects of H_{PNC} and V_{es} . Using Eq. (3.20) in Eq. (3.13), we get

$$(H^{\rm DC} + \lambda H_{\rm PNC})(\sum_{k} a_{k}^{i} |\Phi_{k}\rangle + \lambda \sum_{k} d_{k}^{i} |\overline{\Phi}_{k}\rangle) = E_{i}(\sum_{k} a_{k}^{i} |\Phi_{k}\rangle + \lambda \sum_{k} d_{k}^{i} |\overline{\Phi}_{k}\rangle).$$
(3.21)

Retaining the terms linear in λ

$$\sum_{k} d_{k}^{i} H^{\rm DC} |\overline{\Phi}_{k}\rangle + \sum_{k} a_{k}^{i} H_{\rm PNC} |\Phi_{k}\rangle = E_{i} \sum_{k} d_{k}^{i} |\overline{\Phi}_{k}\rangle.$$
(3.22)

Projecting above equation with $\langle \overline{\Phi}_j |$

$$\sum_{k} d_{k}^{i} \langle \overline{\Phi}_{j} | H^{\mathrm{DC}} | \overline{\Phi}_{k} \rangle + \sum_{k} a_{k}^{i} \langle \overline{\Phi}_{j} | H_{\mathrm{PNC}} | \Phi_{k} \rangle = E_{i} \sum_{k} d_{k}^{i} \langle \overline{\Phi}_{j} | \overline{\Phi}_{k} \rangle.$$
(3.23)

Considering that the CSFs are orthonormal $\langle \overline{\Phi}_j | \overline{\Phi}_k \rangle = \delta_{jk}$, the above equation can be written in the form

$$\sum_{k} d_{k}^{i} \left(H^{\mathrm{DC}} \right)_{\overline{j},\overline{k}} + \sum_{k} a_{k}^{i} \left(H_{\mathrm{PNC}} \right)_{\overline{j},k} = E_{i} d_{k}^{i}.$$
(3.24)

This equation is the perturbed CI equation and as evident from the discussions d_k^i are the unknown quantity.

3.2.1 Linear equation form of PCI

The PCI equation, Eq. (3.24), can be rearranged and written in the more convenient form

$$\sum_{k} \left[E_i \delta_{jk} - \left(H^{\rm DC} \right)_{\overline{j},\overline{k}} \right] d_k^i = \sum_{k} a_k^i \left(H_{\rm PNC} \right)_{\overline{j},k}.$$
(3.25)

This evidently is in the form of matrix equation Ax = B, where d_k^i are equivalent of the unknown x. And, the elements of the matrices A and B are

$$A_{jk} = \left[E_i \delta_{jk} - \left(H^{\text{DC}} \right)_{\overline{j},\overline{k}} \right], \quad \text{and} \quad B_k = a_k^i \left(H_{\text{PNC}} \right)_{\overline{j},k}.$$
(3.26)

The linear equations can then be solved with any of the standard methods. However, as the number of unknowns is in general very large, it is preferable to use more efficient linear equation solvers like *conjugate gradient*. In our implementation of the method, the matrix elements $(H^{\rm DC})_{jk}$ is generated using GRASP92 [54]. The term $(H_{\rm PNC})_{j,k}$ in the *B* matrix are also computed with GRASP92. This way, the angular factors required in the CSF matrix elements are conveniently generated with GRASP92.

3.2.2 E1PNC from PCI wavefunctions

Once the coefficient d_k^i are obtained after solving the PCI equations, we can use it to compute E1PNC. Using Eq. (3.20) in Eq. (7.3)

E1PNC =
$$\langle \Psi_f | \boldsymbol{D} | \overline{\Psi}_i^1 \rangle + \langle \overline{\Psi}_f^1 | \boldsymbol{D} | \Psi_i \rangle,$$

= $\sum_{j,k} \left[a_k^f d_j^i \langle \Phi_k | \boldsymbol{D} | \overline{\Phi}_j \rangle + d_j^f a_k^i \langle \overline{\Phi}_j | \boldsymbol{D} | \Phi_k \rangle \right],$ (3.27)

We implement this method, Eq. (3.27), to calculate the E1PNC transition amplitude for the atomic system Yb.

3.3 Yb E1PNC

To the PNC experiment point of view, the configurations $[Xe]4f^{14}6s^2$, $[Xe]4f^{14}6s6p$ and $[Xe]4f^{14}5d6s$ are of great importance. As the allowed electric dipole transitions are $|6s^{2} {}^{1}S_0\rangle \longrightarrow |5d6s {}^{3}D_2\rangle$ and $|6s^{2} {}^{1}S_0\rangle \longrightarrow |5d6s {}^{3}D_1\rangle$, through the intermediate states ${}^{3}P_1$ and ${}^{1}P_1$.

For $|6s^{2} {}^{1}S_{0}\rangle \longrightarrow |5d6s {}^{3}D_{2}\rangle$ transition, $J_{i} = 0, J_{f} = 2$ and $I = 5/2, F_{i} = I = 5/2$, and the dominant intermediate states are $|6s6p {}^{3}P_{1}\rangle$ and $|6s6p {}^{1}P_{1}\rangle$. Based on Eq. (3.19), the leading order terms in the $H_{\text{PNC}}^{\text{NSD}}$ induced electric dipole transition amplitude are

$$\frac{(\text{E1PNC})_{1S_{0}}^{3D_{2}}}{\frac{\langle 6s5d \ ^{3}D_{2}, F_{f} \| \boldsymbol{D} \| 6s6p \ ^{3}P_{1}, F_{I} \rangle \langle 6s6p \ ^{3}P_{1}, F_{I} \| \boldsymbol{H}_{\text{PNC}}^{\text{NSD}} \| 6s^{2} \ ^{1}S_{0}, F_{i} \rangle}{E_{6s^{2} \ ^{1}S_{0}} - E_{6s6p \ ^{3}P_{1}}} + \frac{\langle 6s5d \ ^{3}D_{2}F_{f} \| \boldsymbol{H}_{\text{PNC}}^{\text{NSD}} \| 6s6p \ ^{1}P_{1}, F_{I} \rangle \langle 6s6p \ ^{1}P_{1}, F_{I} \| \boldsymbol{D} \| 6s^{2} \ ^{1}S_{0}, F_{i} \rangle}{E_{6s5d \ ^{3}D_{2}} - E_{6s6p \ ^{1}P_{1}}}. \quad (3.28)$$

Where the state $|a\rangle \equiv |(I, J_a)F_aM_{F_a}\rangle$, is the hyperfine state and F = I + J, as mentioned earlier, is the hyperfine quantum number. One point to be noted is, the terms with the dipole matrix elements $\langle 6s5d \ ^3D_2 | \mathbf{D} | 6s6p \ ^1P_1 \rangle$ and $\langle 6s6p \ ^3P_1 \| \mathbf{D} \| 6s^2 \ ^1S_0 \rangle$ are not considered as these are spin changing and rather weak. For short notation, we have dropped writing the nuclear spin I = 5/2 and M_F quantum numbers. Using Eq. (C.8), for the hyperfine quantum numbers $F_f = 5/2$, $F_I = 5/2$ and $F_i = 5/2$

$$(\text{E1PNC})_{{}^{1}S_{0}}^{{}^{3}D_{2}} = \frac{\sqrt{210}G_{\text{F}}\mu_{\text{w}}'}{10}(-1)^{5} \left\{ \begin{array}{cc} 5/2 & 1 & 5/2 \\ 1 & 5/2 & 2 \end{array} \right\} \\ \left[\frac{\langle 2 \| \boldsymbol{\alpha} \rho_{N}(\boldsymbol{r}) \| 1 \rangle \langle 1 \| \boldsymbol{D} \| 0 \rangle}{E_{6s5d} \, {}^{3}D_{2} - E_{6s6p} \, {}^{3}P_{1}} + \frac{\langle 2 \| \boldsymbol{D} \| 1 \rangle \langle 1 \| \boldsymbol{\alpha} \rho_{N}(\vec{r}) \| 0 \rangle}{E_{6s^{2}} \, {}^{1}S_{0} - E_{6s6p} \, {}^{3}P_{1}} \right]. (3.29)$$

Similarly, for $|6s^2 {}^1S_0\rangle \longleftrightarrow |5d6s {}^3D_1\rangle$ transition

$$(\text{E1PNC})_{{}^{1}S_{0}}^{{}^{3}D_{1}} = \frac{\sqrt{210}G_{\text{F}}\mu_{\text{w}}'}{10}(-1)^{5} \left\{ \begin{array}{cc} 5/2 & 1 & 5/2 \\ 1 & 5/2 & 1 \end{array} \right\} \\ \left[-\frac{\langle 1 \| \boldsymbol{\alpha}\rho_{N}(\vec{r}) \| 1 \rangle \langle 1 \| \boldsymbol{D} \| | 0 \rangle}{E_{6s5d} \, {}^{3}D_{1} - E_{6s6p} \, {}^{3}P_{1}} + \frac{\langle 1 \| \boldsymbol{D} \| 1 \rangle \langle 1 \| \boldsymbol{\alpha}\rho_{N}(\vec{r}) \| 0 \rangle}{E_{6s^{2} \, {}^{1}S_{0}} - E_{6s6p} \, {}^{3}P_{1}} \right] (3.30)$$

These are the expressions of leading order terms of the $H_{\rm PNC}^{\rm NSD}$ induced dipole transition amplitude in terms of the CI wave functions. In a similar way, an expression of the leading order terms in the PCI method can as well be evaluated.

3.4 Summary of the results

The Table. 3.1 lists the energies of the spin-orbitals, $\langle r \rangle$ and $\langle r^{-1} \rangle$, these are calculated numerically with GRASP92. In the table, the self-consistent field (SCF) energy is also listed as well.

For atomic Yb a systematic study of electron correlation effect is done with Multi-configuration Dirac-Fock (MCDF) and the Configuration interaction (CI) theories. The Table 3.2 lists the the excitation energies in sequence for some of the low-lying states. The first calculation is with the configuration

Spin-orbital	Energy	$\langle r^{-1} \rangle$	$\langle r \rangle$
	Self-consistent field energy -14067.6716		
$1s_{1/2}$	2268.1763	80.5793	0.0196
$2s_{1/2}$	389.4170	19.5344	0.0825
$3s_{1/2}$	90.2277	7.1755	0.2146
$4s_{1/2}$	19.1507	2.9864	0.4806
$5s_{1/2}$	3.0121	1.0091	1.2443
$6s_{1/2}$	0.4136	0.3257	3.7785
$2p_{1/2}$	370.5739	19.4585	0.0685
$3p_{1/2}$	81.9379	7.0673	0.02044
$4p_{1/2}$	15.7493	2.8550	0.4892
$5p_{1/2}$	2.0080	0.8826	1.3928
$6p_{1/2}$	0.3011	0.2549	4.7184
$2p_{3/2}$	332.0058	16.7235	0.0760
$3p_{3/2}$	73.6093	6.3731	0.02180
$4p_{3/2}$	13.8380	2.6292	0.05191
$5p_{3/2}$	1.7809	0.8042	1.5026
$6p_{3/2}$	0.2883	0.2421	4.9557
$3d_{3/2}$	59.6919	6.2820	0.1912
$4d_{3/2}$	8.3275	2.3417	0.5580
$5d_{3/2}$	0.3031	0.4127	3.1958
$3d_{5/2}$	57.8888	6.1138	0.1953
$4d_{5/2}$	7.9737	2.2820	0.5696
$5d_{5/2}$	0.3009	0.4025	3.2552
$4f_{5/2}$	1.0646	1.7768	0.7416
$4f_{7/2}$	1.0061	1.7439	0.7594

Table 3.1: Energies of the core- and valence-orbitals for the atomic Yb^{++} , calculated using Dirac-Fock theory. All values listed are in atomic units.

Configuration	No. of CSF	Energy level	Excitation energy	Exp. result
$\begin{array}{r} 4f^{14}6s^2 + 4f^{14}6s6p \\ + 4f^{14}5d6s \end{array}$	9	$ \begin{array}{r} {}^{1}S_{0} \\ {}^{3}P_{0} \\ {}^{3}P_{1} \\ {}^{3}P_{2} \\ {}^{3}D_{1} \\ {}^{3}D_{2} \\ {}^{1}P_{1} \\ {}^{3}D_{2} \end{array} $	0.0 0.04518 0.04916 0.05669 0.09586 0.09607 0.12046 0.09638	$\begin{array}{c} 0.0\\ 0.07877\\ 0.08198\\ 0.08981\\ 0.11158\\ 0.11278\\ 0.11278\\ 0.11422\\ 0.11514\end{array}$
previous + $4f^{14}6p^2 + 4f^{14}5d^2$ $+4f^{13}6s^25d$	38	$D_{3}^{1}D_{2}^{1}D_{2}^{1}D_{2}^{1}D_{2}^{1}D_{2}^{1}P_{1}^{3}P_{2}^{3}D_{1}^{3}D_{2}^{1}P_{1}^{3}D_{3}^{1}D_{2}^{1}D$	$\begin{array}{c} 0.0\\ 0.06410\\ 0.06745\\ 0.07422\\ 0.11570\\ 0.11590\\ 0.14643\\ 0.11622\\ 0.12122\end{array}$	$\begin{array}{c} 0.11314\\ 0.12611\\ 0.0\\ 0.07877\\ 0.08198\\ 0.08981\\ 0.11158\\ 0.11278\\ 0.11278\\ 0.11422\\ 0.11514\\ 0.12611\\ \end{array}$
$\begin{array}{l} {\rm previous} + \\ 4f^{14}6p^2 + 4f^{14}5d^2 \\ + 4f^{13}6s^26p + 4f^{13}6s^25d \end{array}$	47	D_{2} $^{1}S_{0}$ $^{3}P_{0}$ $^{3}P_{1}$ $^{3}P_{2}$	$0.0 \\ 0.06398 \\ 0.06734 \\ 0.07410$	0.0 0.07877 0.08198 0.08981

Table 3.2: Configuration interaction calculation of the excitation energies for some of the low-lying levels in atomic Yb. Values listed are in atomic unit.

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Configuration	No. of CSF	Energy level	Excitation energy	Exp. result
		2		
		${}^{3}D_{1}$	0.11538	0.11158
		${}^{3}D_{2}$	0.11574	0.11278
		${}^{1}P_{1}$	0.14602	0.11422
		${}^{3}D_{3}$	0.11631	0.11514
		${}^{1}D_{2}$	0.12124	0.12611
provious $14f^{145}d6n$	61	1 C	0.0	0.0
previous $\pm 4j$ 5 <i>a</i> 0 <i>p</i>	01	3D	0.0	0.0
		Γ_0 3 D	0.00101 0.06412	0.07077
		3D	0.00412	0.08198
		Γ_2	0.07100 0.11670	0.00901
		$^{\circ}D_{1}$	0.11070	0.11100 0.11070
		$^{\circ}D_{2}$	0.11089	0.11278
		${}^{1}P_{1}$	0.11420	0.11422
		$^{\circ}D_{3}$	0.11723	0.11514
		${}^{1}D_{2}$	0.12155	0.12611
previous $+4f^{13}6s6p5d$	163	${}^{1}S_{0}$	0.0	0.0
1 0 1		${}^{3}P_{0}$	0.06117	0.07877
		${}^{3}P_{1}$	0.06428	0.08198
		${}^{3}P_{2}^{1}$	0.07133	0.08981
		${}^{3}D_{1}^{2}$	0.11611	0.11158
		${}^{3}D_{2}$	0.11631	0.11278
		${}^{1}P_{1}^{2}$	0.11281	0.11422
		${}^{3}D_{3}$	0.11664	0.11514
		${}^{1}D_{2}^{0}$	0.12179	0.12611

 $4f^{14}6s^2 + 4f^{14}6s6p + 4f^{14}5d6s$. There can be at the most 9 CSFs constructed form this and all of these are optimized. However, as evident from the table, the energy level sequence is inconsistent with the experimental data. The state ${}^{1}P_{1}$ appears above the all other states. However it should lies between the states ${}^{3}D_{2}$ and ${}^{3}D_{3}$. In addition, the excitation energies deviate from the experimental data by $\approx 36\text{-}42\%$, $\approx 14\text{-}16\%$ and $\approx 6\%$ for ${}^{3}P$, ${}^{3}D$ and ${}^{1}P$ respectively.

In the next step of the calculation, the configurations $4f^{14}6p^2 + 4f^{14}5d^2 + 4f^{13}6s^25d$ added to the previous one. In this case there is no change in the energy level sequence. However there is significant change in the excitation energies. The discrepancies are now $\approx 17\text{-}19\% \approx 1\text{-}4\%$, $\approx 28\%$ and $\approx 4\%$ for ${}^{3}P$, ${}^{3}D$, ${}^{1}P$ and ${}^{1}D$ respectively. In the third step, the odd-parity configuration $4f^{13}6s^{2}6p$ added. However, the changes in the energy occur at the fourth place of the decimal.

In the next step of the calculation, the odd-parity configuration $4f^{14}5d6p$ is added to the previous one. This is a configuration which mixes very strongly with the $4f^{14}6s6p$, and as result there is significant change in the energy level sequence. As noticeable from the Table, the state ${}^{1}P_{1}$ is shifted below ${}^{3}D_{1}$. This points to strong mixing between the the two odd-parity configurations. The excitation energy of the ${}^{3}P$ and ${}^{3}D$ states deteriorate, however there is excellent improvement in the case of ${}^{1}P_{1}$. The corresponding discrepancies are $\approx 20\text{-}23\%$, $\approx 2\text{-}6\%$, $\approx 0.04\%$ and $\approx 4\%$ in ${}^{3}P$, ${}^{3}D$, ${}^{1}P$ and ${}^{1}D$ respectively.

Chapter 4

Coupled-cluster theory of closed-shell and one-valence atoms

The coupled-cluster theory [47] is one of the best many-body methods to incorporate electron correlation effects in atomic calculations. It was first developed in nuclear many body physics [68, 69] and in recent times has been used with great success in nuclear [70], atomic [71, 72], molecular [73] and condensed matter [74] calculations. In the literature several authors refer to coupled-cluster as all-order method. A description of the all-order method and applications are given in Ref [75]. A recent review [66] provides an excellent overview of recent developments and different variations.

CCT is a non-perturbative many-body theory which account for the correlation effects in terms of cluster operators, which transforms a reference state to state of different excitations. The cluster operators are solutions of equations consisting of only connected terms and generates the linked wave function through an exponential operator. In the context of diagrammatic analysis of many-body perturbation theory, coupled-cluster theory is equivalent to a selective evaluation of the connected diagrams to all orders. Then casting the disconnected but linked diagrams as products of connected diagrams.

The Figs. 4.1 and 4.2 show a schematic representation of the single and double excitation cluster operators. It is possible to obtain triple and quadruple excitations as product of these operators. In other words, even when the cluster operator is restricted to singles and doubles it is possible to incorporate electron correlation from triple and quadrupole excitations. This is because of the exponential nature of the wave operator in CCT.

This chapter is organized as follows. In Sec. II the closed-shell CCT theory is described. Properties calculations of the closed-shell systems is also given. The CCT and the working equations of open-shell one-valence systems



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Figure 4.1: Diagrammatic representation of the all-order single excitations from occupieds to the virtuals.



Figure 4.2: Diagrammatic representation of the all-order double excitations from occupieds to the virtuals.

is elaborated in Sec. III. Like in closed-shell case, this section also describes the properties calculations for one-valence systems. Sec. IV gives a description of CCT of two-valence system and provides the details of properties calculations.

4.1 Closed-shell system

The main purpose of the method is to solve the equation

$$H^{\rm DC}|\Psi_0\rangle = E_0|\Psi_0\rangle,\tag{4.1}$$

for wave function $|\Psi_0\rangle$ and energy E_0 .

The exact atomic wave function, Eq. (4.1), in the CC theory is defined as

$$|\Psi_0\rangle = e^{T^{(0)}}|\Phi_0\rangle, \qquad (4.2)$$

where $T^{(0)}$ is the cluster operator and $|\Phi_0\rangle$ is the Dirac- Fock reference state, described in the Chapter. II., of closed-shell system. The superscript is a tag


Figure 4.3: Representation of unperturbed single and double cluster operators. Incoming(downwards) arrow represent the hole state and outgoing(upwards) arrow is to represent the particle state.

to identify cluster operators arising from different perturbations. The tag 0 here indicates that no external perturbation is applied. For the case of an N electron system, the cluster operator, in principle, is

$$T^{(0)} = \sum_{i=1}^{N} T_i^{(0)}.$$
(4.3)

In closed shell systems, the single and double provide a good approximation of the exact ground state. The cluster operator is then $T^{(0)} = T_1^{(0)} + T_2^{(0)}$ and is referred to as the coupled-cluster single and double (CCSD). The cluster operators in the second quantized notations are

$$T_1^{(0)} = \sum_{a,p} t_a^p a_p^\dagger a_a , \quad \text{and} \quad T_2^{(0)} = \frac{1}{2!} \sum_{a,b,p,q} t_{ab}^{pq} a_p^\dagger a_q^\dagger a_b a_a.$$
(4.4)

These act on the reference state as

$$T_1^{(0)}|\Phi_0\rangle = \sum_{a,p} t_a^p |\Phi_a^p\rangle , \quad \text{and} \quad T_2^{(0)}|\Phi_0\rangle = \frac{1}{2!} \sum_{a,b,p,q} t_{ab}^{pq} |\Phi_{ab}^{pq}\rangle.$$
(4.5)

The indices $abc \ldots$ and $pqr \ldots$ represent the core and virtual states respectively. Here, t_a^p and t_{ab}^{pq} are the single and double cluster amplitudes respectively, and $|\Phi_a^p\rangle$ and $|\Phi_{ab}^{pq}\rangle$ are the singly and doubly excited determinants respectively. As mentioned in the Chapter. II., these differ from the reference state in having one and two electrons respectively from the cores are replaced by the virtuals.

Subtracting $\langle \Phi_0 | H | \Phi_0 \rangle$ from both sides of Eq. (4.1) and define the normal form of the operator, $H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle$. The equation is then

$$H_{\rm N}|\Psi_0\rangle = \Delta E|\Psi_0\rangle,\tag{4.6}$$

where ΔE is the difference of the exact energy and the self-consistent field energy, $E - \langle \Phi_0 | H | \Phi_0 \rangle$. It is referred to as the correlation energy of the system. Substituting the CCT wave function from Eq. (4.2), we get

$$H_{\rm N}e^{T^{(0)}}|\Phi_0\rangle = \Delta E e^{T^{(0)}}|\Phi_0\rangle.$$
 (4.7)

Operating with $e^{-T^{(0)}}$ and projecting on the excited states $\langle \Phi_a^p |$ and $\langle \Phi_{ab}^{pq} |$, we get the coupled-cluster equations of the singles and doubles cluster operators as

$$\langle \Phi_a^p | H_{\rm N} | \Phi_0 \rangle = 0, \tag{4.8}$$

$$\langle \Phi_{ab}^{pq} | H_{\rm N} | \Phi_0 \rangle = 0. \tag{4.9}$$

Where, $\bar{H}_{\rm N} = e^{-T^{(0)}} H_{\rm N} e^{T^{(0)}}$ is the similarity transformed or dressed Hamiltonian. Following the Wick's theorem the structure of $\bar{H}_{\rm N}$ is

$$\bar{H}_{N} = H_{N} + \{\bar{H}_{N}T^{(0)}\} + \frac{1}{2!}\{\bar{H}_{N}T^{(0)}T^{(0)}\} + \frac{1}{3!}\{\bar{H}_{N}T^{(0)}T^{(0)}T^{(0)}\} + \frac{1}{4!}\{\bar{H}_{N}T^{(0)}T^{(0)}T^{(0)}T^{(0)}\}, \quad (4.10)$$

The single and double cluster amplitudes are solutions of Eqs. (4.8) and (4.9) respectively.

4.1.1 Linearized coupled-cluster

An approximation often used as a starting point of coupled-cluster calculations is to retain only the first two terms in the dressed operator \bar{H}_N . We then can write

$$\bar{H}_{\rm N} = H_{\rm N} + \{ \overline{H_{\rm N}} T^{(0)} \}.$$
(4.11)

The coupled-cluster equations, Eq. (4.8)-(4.9), are then a pair of linear equations

$$\langle \Phi_a^p | H_{\rm N} + \{ H_{\rm N} T^{(0)} \} | \Phi_0 \rangle = 0,$$
 (4.12)

$$\langle \Phi_{ab}^{pq} | H_{\rm N} + \{ \dot{H}_{\rm N} \dot{T}^{(0)} \} | \Phi_0 \rangle = 0.$$
 (4.13)

In the CCSD approximation $T^{(0)} = T_1^{(0)} + T_2^{(0)}$, these equations are

$$\langle \Phi_{a}^{p} | \{ H_{N} T_{1}^{(0)} \} + \{ H_{N} T_{2}^{(0)} \} | \Phi_{0} \rangle = -\langle \Phi_{a}^{p} | H_{N} | \Phi_{0} \rangle$$
(4.14)

$$\langle \Phi_{ab}^{pq} | \{ H_N T_1^{(0)} \} + \{ H_N T_2^{(0)} \} | \Phi_0 \rangle = -\langle \Phi_{ab}^{pq} | H_N | \Phi_0 \rangle.$$
(4.15)

These are the linearized coupled-cluster equations of single and double cluster amplitudes. The diagrams contributing to these equations are shown in the Figs. 4.4 and 4.5 respectively. The Eqs. (4.14) and (4.15) can be written as the matrix equation

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} t_1 \\ t_2 \end{pmatrix} = - \begin{pmatrix} H_{10} \\ H_{20} \end{pmatrix}, \qquad (4.16)$$

where $H_{11} = \langle \Phi_a^p | H_N | \Phi_b^s \rangle$, $H_{12} = \langle \Phi_a^p | H_N | \Phi_{bc}^{st} \rangle$ and so on. The equations form a set of coupled linear equations and is solved using standard or specialized linear algebra solvers.



Figure 4.4: Coupled-cluster diagrams which contribute to the unperturbed single cluster operator, $T_1^{(0)}$, in the linearized coupled-cluster theory. Dashed line represent the residual coulomb interaction and the lower solid line is to represent the cluster operator.



Figure 4.5: Coupled-cluster diagrams which contribute to the unperturbed double cluster operator, $T_2^{(0)}$, in the linearized coupled-cluster theory.

4.1.2 Correlation Energy from CCT

Operating Eq. (4.7) with $e^{-T^{(0)}}$ and projecting on the model wave function $\langle \Phi_0 \rangle$, we get the ground state correlation energy of the closed-shell system as

$$\Delta E = \langle \Phi_0 | \overline{H}_N | \Phi_0 \rangle = \langle \Phi_0 | \{ \overline{H}_N T_1^{(0)} \} + \{ \overline{H}_N T_2^{(0)} \} + \{ \overline{H}_N T_1^{(0)} T_1^{(0)} \} | \Phi_0 \rangle.$$
(4.17)

The diagrams which contribute to ΔE are obtained by applying Wick's theorem such that there are no free lines after the contraction. These are shown in the Fig. 4.6. The dominant contributions arise from the diagrams (a) and (b), which is expected as the doubles cluster amplitudes are larger in value than the singles. Diagram (e) has zero value if Dirac-Fock orbitals are used.



Figure 4.6: Coupled-cluster diagrams contributing to the correlation energy. Dashed lines represent the residual Coulomb interaction and the solid lines at the bottom are to represent the coupled-cluster operators. Diagram (e) will not contribute if Dirac-Fock orbitals are used in the calculations.



Figure 4.7: Representation of the approximate triple cluster operators.

4.1.3 Approximate triples

The inclusion of T_3 , triples cluster operator, in CCT is computationally expensive. However, the dominant triples contribution can be accounted as a contraction of T_2 and H_N . This is in literature referred to as the approximation triples [76, 77]. The contribution to correlation energy from approximate triples is

$$(\Delta E)_{\text{triples}} = \langle \Phi_0 | \{ H_N H_N H_N T \} | \Phi_0 \rangle.$$
(4.18)

Selected diagrammatic representation of these are shown in Fig. 4.8. This shows that the correlation energy contribution from the approximate triple cluster amplitudes involve three-orders of the perturbation and one order of the cluster operator T. For this reason the contribution is expected to be very small. And this is what is observed from the results of actual calculations.

As shown in Fig. 4.7, there are two categories of triples. First is $H_{\rm N}$ contracted with $T^{(0)}$ through a hole line, and second contracted through a particle line. The diagrams contributing to the correlation energy are obtained as the contraction of two orders of $H_{\rm N}$ with the approximate triple cluster operators. There are several diagrams contributing to the Eq. (4.18), and as example two diagrams arising from each category of the approximate triples are shown in Fig. (4.8). To simplify in the computational implementation, these diagrams are separated into three categories based on the number of internal lines. These are: two particle and two hole internal lines (2p-2h), three particle and one hole internal lines (3p-1h), and one particle and three hole internal lines (1p-3h). Contributions from each of these categories are listed in the result section.

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Figure 4.8: Representation of the correlation energy diagrams arising from the approximate triple cluster operators.



Figure 4.9: Energy level diagram showing the excitations of electrons from core to the valence and virtuals, and from valence to the virtuals, for one-valence atoms.

4.2 One-valence systems

In this section we describe the CCT of one-valence systems. For such systems the Schroedinger equation to be solved is

$$H^{\rm DC}|\Psi_v\rangle = E_v|\Phi_v\rangle,\tag{4.19}$$

where $|\Psi_v\rangle$ is the exact state and E_v is corresponding exact energy. In singlevalence systems there is a valence orbital in addition to the cores and virtuals. An excitation of electron is then from the cores to the valence or virtuals or from the valence to the virtuals. As shown in Fig. 4.9, the former is accounted by the closed-shell cluster operator T and for the later, a new class of cluster operator S is introduced. These are referred to as the open-shell cluster operator.

The exact wave function in one-valence CCT is

$$|\Psi_v\rangle = e^{T+S} |\Phi_v\rangle. \tag{4.20}$$

The operator T, described in the previous section, is the cluster operator of the closed-shell sector. In the Fock space coupled-cluster theory of single valence

this is evaluated first. The newly introduced operator S is the coupled-cluster operator of the one-valence sector. $|\Phi_v\rangle$ is the one-valence reference state obtained by adding an electron to the closed-shell reference state. That is

$$|\Phi_v\rangle = a_v^{\dagger}|\Phi_0\rangle. \tag{4.21}$$

For single valence atoms

$$e^S = 1 + S,$$
 (4.22)

since there is only one valence electron the higher order cluster operators in the exponential do not contribute. Using Eq. (4.22) in Eq. (4.20) we can write

$$|\Psi_v\rangle = e^T (1+S) |\Phi_v\rangle. \tag{4.23}$$

For an N electron atom

$$T = \sum_{i=1}^{N-1} T_i$$
, and $S = \sum_{i=1}^{N} S_i$. (4.24)

Here the summation index of the T is up to the N-1 core electrons, where as S is up to N to include the valence electron. Following the the closed-shell case, in CCSD approximation the open-shell cluster operator $S = S_1 + S_2$. In the second quantized representation these are

$$S_1 = \sum_p s_v^p a_p^{\dagger} a_v$$
, and $S_2 = \sum_{a,p,q} s_{va}^{pq} a_p^{\dagger} a_q^{\dagger} a_a a_v$. (4.25)

Diagrammatic representation of S_1 and S_2 are shown in Fig. 4.10. These generate the singly and doubly excited determinants respectively, after acting on the reference state $|\Phi_v\rangle$. That is



Figure 4.10: Diagrammatic representation of open shell cluster operators. The orbital lines with double arrows indicate valence and single up (down) arrow indicate particle (hole) states.

Using normal-ordered form of the Hamiltonian, $H_{\rm N} = H - \langle \Phi_v | H \Phi_v \rangle$, Eq. (4.19) can further be written as

$$H_{\rm N}|\Psi_v\rangle = \Delta E_v \Psi_v\rangle.$$
 (4.27)

Where, in analogy to the closed-shell atoms case, $\Delta E_v = E_v - E_v^{(0)}$, is correlation energy of the one-valence atoms. Putting the coupled-cluster wave function, defined in Eq. (4.23), to the Eq. (4.27) and applying e^{-T} on both sides of the equation, we get

$$\bar{H}_{\rm N}(1+S)|\Phi_v\rangle = \Delta E_v(1+S)|\Phi_v\rangle, \qquad (4.28)$$

where $\bar{H}_{\rm N}$ is the dressed Hamiltonian defined in Eq. 4.10. The coupled-cluster amplitude equations for singles and doubles are obtained after projecting Eq. (4.28) on singly and doubly replaced states $\langle \Phi_v^p |$ and $\langle \Phi_{va}^{pq} |$.

$$\langle \Phi_v^p | \bar{H}_N(1+S) | \Phi_v \rangle = \Delta E_v \langle \Phi_v^p | S_2 | \Phi_v^p \rangle, \qquad (4.29)$$

$$\langle \Phi_{va}^{pq} | \bar{H}_{N}(1+S) | \Phi_{v} \rangle = \Delta E_{v} \langle \Phi_{va}^{pq} | S_{2} | \Phi_{v} \rangle.$$

$$(4.30)$$

Here we have used $\langle \Phi_v^p | \Phi_v \rangle = 0$ and $\langle \Phi_{va}^{pq} | \Phi_v \rangle = 0$, as singly and doubly excited determinants $\langle \Phi_v^p |$ and $\langle \Phi_{va}^{pq} |$ are orthogonal to the reference state $| \Phi_v \rangle$. Using Wick's theorem above equations can further be reduced to the form

$$\langle \Phi_v^p | \bar{H}_N + \{ \dot{\bar{H}}_N S_1 \} + \{ \dot{\bar{H}}_N S_2 \} | \Phi_v \rangle = E_v^{\text{att}} \langle \Phi_v^p | S_1 | \Phi_v \rangle, \qquad (4.31)$$

$$\langle \Phi_{va}^{pq} | \bar{H}_N + \{ \dot{\bar{H}}_N S_1 \} + \{ \dot{\bar{H}}_N S_2 \} | \Phi_v \rangle = E_v^{\text{att}} \langle \Phi_{va}^{pq} | S_2 | \Phi_v \rangle, \qquad (4.32)$$

where E_v^{att} is the attachment energy of the valence electron v.

4.2.1 Energy from CCT

To obtain the energy eigenvalue E_v of the state $|\Psi_v\rangle$, project Eq. (4.19) on the state $\langle \Phi_v |$ after putting the CC wave function from Eq. (4.23). We then get

$$\langle \Phi_v | \bar{H}(1+S) | \Phi_v \rangle = E_v, \tag{4.33}$$

here we have used $\langle \Phi_v | S | \Phi_v \rangle = 0$, as S acting on the reference state produces an excited state which is orthogonal to the reference state. Using the normalordered Hamiltonian defined earlier, above equation becomes

$$\langle \Phi_v | \bar{H}_N \left(1 + S \right) | \Phi_v \rangle = \Delta E_v^{N, \text{corr}}, \qquad (4.34)$$

where $\Delta E_v^{N,\text{corr}}$ is the correlation energy of N-electron (one-valence) system. The attachment energy introduced in the CC equations is expressed in terms of the correlation energies of N- and (N-1)-electron systems. That is

$$E_v^{\text{att}} = \Delta E_v^{N, \text{corr}} - \Delta E_v^{N-1, \text{corr}} + \epsilon_v,$$

= $\Delta E_v^{\text{att}} + \epsilon_v.$ (4.35)

Where, ϵ_v is the single electron energy of the valence electron. And ΔE_v^{att} , = $\Delta E_v^{N,\text{corr}} - \Delta E_v^{N-1,\text{corr}}$, is the difference of correlation energy of the closed-shell sector from that of the open-shell sector. The contributing diagrams to ΔE_v^{att} are shown in the Fig. 4.11.



Figure 4.11: Diagrams which contribute to ΔE_v^{att} . The dashed lines represent the residual Coulomb interaction. And at the bottom solid lines are to represent the cluster operator.

4.3 Properties from CC wave function

In this section we describe the procedures for atomic properties calculations using CC wave functions, calculated in the previous sections. For this, we consider, for example, calculation of the hyperfine structure constants and the electric dipole transition amplitudes. There is an important difference between these two properties, first is the expectation of the hyperfine interaction, and second is the matrix element of the electric dipole operator between two different states.

4.3.1 Hyperfine Structure constants

The hyperfine splitting is the outcome of the interaction between the nuclear electromagnetic moments and the electromagnetic fields of the atomic electrons. The energy shift, due to the hyperfine splitting, is typically orders of magnitude smaller than the fine structure splitting. The hyperfine structure (HFS) constants are considered to be important parameters to measure the energy shifts. In this case F(I + J) is a good quantum number, and hence the HFS splitting is associated with the coupled states $|(IJ)FM_F\rangle$, I and J are the nuclear spin and total angular momentum quantum numbers respectively.

4.3.1.1 Hyperfine interaction Hamiltonian

The general form of the hyperfine interaction Hamiltonian is [46, 78]

$$H_{\rm hfs} = \sum_{i} \sum_{k,q} (-1)^{q} t_{q}^{k}(\hat{\mathbf{r}}_{i}) T_{-q}^{k}, \qquad (4.36)$$

where $t_q^k(\mathbf{r})$ and T_q^k are irreducible tensor operators of rank k in the electron and nuclear spaces respectively. From the parity selection rule of the electric multipole transitions, $\pi(Ek) = (-1)^k$, only even multipoles are allowed. Following this, the allowed multipole for the electric quadrupole transition is k = 2. Similarly, following the selection rule, $\pi(Mk) = (-1)^{k+1}$, for the magnetic multiples transitions, the allowed multipole for magnetic dipole transition is k = 1. For magnetic dipole hyperfine, the explicit form of the electronic and nucleonic parts of the tensor operators, in Eq. (4.36), are

$$t_q^1(\mathbf{r}) = \frac{-i\sqrt{2}[\boldsymbol{\alpha} \cdot \mathbf{C}_1(\hat{\mathbf{r}})]_q}{cr^2}, \quad \text{and} \quad T_q^1 = \mu_q.$$
(4.37)

where, $\mathbf{C}_1(\hat{\mathbf{r}})$ is a rank one tensor operator in electron space and μ_q is a component of $\boldsymbol{\mu}$, the nuclear magnetic moment operator. Then the nuclear moment is the expectation value of $\boldsymbol{\mu}$ in the stretched state $\boldsymbol{\mu} = \langle II | \mu_0 | II \rangle$. Similarly, for the electric quadrupole hyperfine

$$t_q^2(\mathbf{r}) = -\frac{C_q^2(\hat{r})}{r^3}, \quad \text{and} \quad T_q^2 = Q_q.$$
 (4.38)

Where, Q_q is the irreducible tensor operator of rank 2. For one valence systems, the magnetic dipole and electric quadrupole HFS constants are

$$a = \frac{g_I \mu_N}{j_v} \begin{pmatrix} j_v & 1 & j_v \\ -j_v & 0 & j_v \end{pmatrix} \langle n_v \kappa_v \| t^1 \| n_v \kappa_v \rangle.$$
(4.39)

$$b = 2Q \begin{pmatrix} j_v & 2 & j_v \\ -j_v & 0 & j_v \end{pmatrix} \langle n_v \kappa_v \| t^2 \| n_v \kappa_v \rangle.$$

$$(4.40)$$

Here, $g_I \ (\mu = g_I I \mu_N)$ is the gyro-magnetic ratio and μ_N is the nuclear magnetron. For details of the derivation see the reference [46]. The reduced matrix elements $\langle n_v \kappa_v || t^1 || n_v \kappa_v \rangle$ and $\langle n_v \kappa_v || t^2 || n_v \kappa_v \rangle$ can further be evaluated by using relativistic single-electron wave function. The details about the derivation are given in the Appendix.D.

4.3.1.2 HFS constants from CC wave function

The general expression of the HFS constants, for one-valence atomic systems, is written as

$$A = \frac{\langle \Psi_v | H_{\rm hfs} | \Psi_v \rangle}{\langle \Psi_v | \Psi_v \rangle}.$$
(4.41)

Where, $|\Psi_v\rangle$ is the CC wave function. The HFS constant A, in the Eq. (4.41), can be either magnetic dipole or electric quadrupole constants depending on the form of the hyperfine interaction Hamiltonian H_{HFS} . Using the CC wave function from Eq. (4.23), the numerator of the Eq. (4.41) is

Where, $\tilde{H}_{\rm hfs} = e^{T^{\dagger}} H_{\rm hfs} e^{T}$ is the dressed hyperfine operator. The factor of two in the second term on the right hand side accounts for $\tilde{H}_{\rm hfs}S$ as $S^{\dagger}\tilde{H}_{\rm hfs} = \tilde{H}_{\rm hfs}S$. The dressed hyperfine operator can be expanded as

$$\tilde{H}_{\rm hfs} = H_{\rm hfs} e^T + \sum_{n=1}^{\infty} \frac{1}{n!} \left(T^{\dagger}\right)^n H_{\rm hfs} e^T.$$
(4.43)



Figure 4.12: Representation of effective one- and two-body dressed properties operators.



Figure 4.13: The leading diagrams contributing to the hyperfine structure constants in Eq. (4.42). The dashed lines terminated with a circle represent hyperfine interaction.

As evident from Eq. (4.43), the dressed properties operator $\tilde{H}_{\rm hfs}$ is a non terminating series. And it is therefore not possible to incorporate all the terms in the calculations. In the actual calculations, a truncated expression consisting of terms up to the second-order in T is considered. In this approximation

$$\tilde{H}_{\rm hfs} \approx H_{\rm hfs} + H_{\rm hfs}T + T^{\dagger}H_{\rm hfs} + T^{\dagger}H_{\rm hfs}T.$$
(4.44)

The normalization factor, denominator in Eq. (4.41), in the HFS constants expression is expressed as

$$\langle \Psi_v | \Psi_v \rangle = \langle \Phi_v | (1 + S^{\dagger}) e^{T^{\dagger}} e^T (1 + S) | \Phi_v \rangle.$$
(4.45)

In the actual implementation, like in $\hat{H}_{\rm hfs}$, only terms up to the second-order in T are included. The contribution from the higher order terms is negligibly small.

4.3.2 Dipole transition amplitudes from CC wave function

An atom in the initial state $|\Psi_i\rangle$ may undergo a transition to another state $|\Psi_f\rangle$ while interacting with electromagnetic fields provided incident photon is

resonant. Among various possibilities, transitions arising from electric dipole is the most dominant radiative transition. A quantity which is closely associated with transition properties is the transition amplitude, the matrix element of the electromagnetic multipole operator. However, it is more convenient to calculate the reduced matrix element, from which transition amplitude between specific magnetic quantum numbers may be valuated.

The reduced matrix element of the dipole operator D between the initial and final states is

$$D_{fi} = \frac{\langle \Psi_f \| D \| \Psi_i \rangle}{\sqrt{\langle \Psi_f | \Psi_f \rangle \langle \Psi_i | \Psi_i \rangle}}.$$
(4.46)

It is non-zero when the two states are of opposite parity, as D is an odd parity operator. Using CC wave function from Eq. (4.23),

where, $|\Phi_v\rangle$ and $|\Phi_w\rangle$ are the initial and final reference states of the system with valence electron v and w respectively. Here, \tilde{D} is the dressed dipole operator, it has the form

$$\tilde{D} = De^T + \sum_{n=1}^{\infty} \frac{1}{n!} \left(T^{\dagger}\right)^n De^T.$$
(4.48)

Like in HFS, in calculations \tilde{D} is approximated as

$$\widetilde{D} \approx D + DT + T^{\dagger}D + T^{\dagger}DT.$$
 (4.49)

The contributing diagrams to Eq. (4.47) are topologically similar to $H_{\rm HFS}$. The only difference is **D** replaces the hyperfine operator.

4.3.3 Properties to all order

The properties calculation discussed in the previous section is based on the truncated form of the dressed properties operator. In this section we demonstrate a scheme, we have developed, to incorporate the effects of all-order T in the dressed properties operator. This is desirable for the properties calculations with accuracy level commensurate with the experimental data. This is done by grouping the diagrams arising from the dressed operator into different level of excitation (*loe*) and the higher order diagrams are then evaluated iteratively. Here, *loe* is the number of core or valence electrons replaced with virtual electrons. For example, the diagrams in Fig. 4.14 have *loe* one. In each of these diagrams, one core electron is replaced by a virtual electron.

To demonstrate the proposed scheme consider the example of the *loe* one diagrams. We start with the first term, $H_{\rm hfs}e^T$, in Eq. (4.43). Considering the contribution from the diagrams which have *loe* one, we can write

$$\left(H_{\rm hfs}e^T\right)_1 = \left(H_{\rm hfs} + H_{\rm hfs}T + \frac{1}{2}H_{\rm hfs}TT\right)_1. \tag{4.50}$$

The subscript 1 here is represents the *loe* of the contributing terms. There are six diagrams which contribute to the above equation and these are shown in the first row of the Fig. 4.14. These diagrams constitute an effective operator with the *loe* one, which is the starting point of the iterative calculation. The diagrams of the next iteration are obtained by sandwiching this effective operator between the closed-shell cluster operators of equal but opposite *loe*, so that net *loe* remains one. The equivalent algebraic expression of the next iteration is

$$\left(T^{\dagger}H_{\rm hfs}e^{T}\right)_{1} = \sum_{i} \left[T_{i}^{\dagger}\left(H_{\rm hfs} + \frac{1}{2}H_{\rm hfs}T + \frac{1}{6}H_{\rm hfs}TT\right)T_{i}\right]_{1}^{\rm conn},\qquad(4.51)$$

In the CCSD approximation the index *i* runs from 1 to 2. In this case, however, we don not consider the terms (diagrams) arising due to the single cluster operator T_1 as the contributions can be neglected in comparison to the T_2 operators. The other superscript *conn*, in the above equation, imply only the connected diagrams contribute. There are eight diagrams which contribute to this iteration and these are shown as the diagrams in the second and third row of the Fig. 4.14.

Following the above discussions we can then write the general expression as

$$\left(T^{\dagger^{n}}H_{\rm hfs}e^{T}\right)_{1} = \sum_{i} \left[T_{i}^{\dagger}\left(T^{\dagger^{n-1}}H_{\rm hfs}e^{T}\right)_{1}T_{i}\right]_{1}^{\rm conn}.$$
(4.52)

This is an iterative equation and it is possible to evaluate it order by order to convergence. The sum of all the contributions is equivalent to calculating the effective operator

$$\mathcal{H}_1 = (e^{T^{\dagger}} H_{\text{hfs}} e^T)_1. \tag{4.53}$$

From Eq. (4.42), this contribute to the hyperfine structure through the term $S_2^{\dagger}\mathcal{H}_1$. At the lowest level, the contributing hyperfine diagrams are shown as Fig. 4.13(j-k). Using the same terminology described here, as an example, for *loe* one it is possible to extend the method for to higher *loe*.

4.4 Summary of the results

In this section we present and analyze the results calculated using coupledcluster theories for closed-shell and one valence atomic systems. In the context



Figure 4.14: Diagrammatic representation of the iterative equation to calculate the *loe* one effective hyperfine operator $H_{\rm hfs1}^{\rm eff}$. The iteration is implemented with the T_2^{\dagger} and T_2 .

of closed-shell atoms, we have done a detail study of the correlation energy. We also examine the contribution from the approximate triples to the correlation energy. For the one-valence atoms, however, apart from correlation energy, the HFS constants and the electric-dipole (E1) transition amplitudes are also studied. Like in the MBPT case, here also we have employed the even tempered Gaussian-type basis functions. We have used the same basis set parameters listed earlier.

4.4.1 Correlation energy of closed-shell atoms

The coupled-cluster results of the correlation energy of the inert gas atoms are presented in the Table. 4.1. Contribution from the nonlinear terms in the coupled-cluster is tabulated separately. An optimal basis set is chosen based on the results of a series of calculations, such that the basis set is suitable for CCSD computations. Unlike in MBPT, the virtuals space includes orbitals up to the h symmetry only. Contributions from the higher symmetry orbitals are negligible. In addition, it is computationally expensive as the number of cluster amplitudes scale as $n_v^2 n_c^2$, n_v and n_c are the number of virtual and core orbitals respectively.

To account for the correlation energy contribution from the higher symmetries orbitals, not included in the CCSD calculations, we resort to the second order correlation energy. For this we calculate $E_{\rm corr}^{(2)}$ with the basis set chosen in CCSD calculations and subtract from the converged $E_{\rm corr}^{(2)}$ described in Chapter. II. The estimated correlation energy is the sum of this difference and CCSD ΔE . Our estimated value of 0.3882 for Ne is in excellent agreement with the experimental value, which lies in the range 0.385 and 0.390 [60, 67]. The contribution from the nonlinear terms is found to be 0.6%, 0.8%, 0.08% and 0.03%. It must be mentioned that, though the difference in ΔE is small,

Atom	Active Orbitals	$\Delta E(\text{ccsd})$		
		Linear	Nonlinear	
Ne	17s10p10d9f9g8h	-0.3783	-0.3760	
	18s11p11d10f10g9h	-0.3805	-0.3782	
	Estimated	-0.3905	-0.3882	
Ar	17s11p11d9f9g9h	-0.6884	-0.6829	
	18s12p12d10f10g10h	-0.7001	-0.6945	
	Estimated	-0.7258	-0.7202	
Kr	22s13p11d9f9g9h	-1.5700	-1.5688	
	23s14p12d10f10g10h	-1.6730	-1.6716	
	Estimated	-1.8480	-1.8466	
Xe	23s14p12d10f10g10h	-2.5500	-2.5509	
	24s15p13d11f11g11h	-2.6874	-2.6881	
	Estimated	-2.9973	-2.9979	

Table 4.1: Correlation energy using coupled-cluster theory for inert gas atoms. All the values are in atomic units.

Table 4.2: Correlation energy contributions from the approximate triples in the coupled-cluster theory. All the values are in atomic units.

Atom	Basis size		ΔE	
		2p-2h	1p-3h	3p-1h
Ne	18s11p11d10f10g9h	0.00672	-0.00145	-0.00164
Ar	18s12p12d10f10g10h	0.00805	-0.00066	-0.00192
Kr	22s13p11d9f9g9h	0.01546	-0.00171	-0.00305
Xe	19s15p10d9f5g2h	0.02011	-0.00148	-0.00260

the computational cost of non-linear CCSD is far higher than the linearized CCSD calculations.

The correlation energy contributions arising from the approximate triples are listed in Table. 4.2. As discussed in the previous sections, the correlation energy diagrams from the approximate triples are grouped into three classes. In the actual calculation, we incorporate eight diagrams from 2p-2h and two each from 3p-1h and 1p-3h categories. Since we include only few correlation energy diagrams it is difficult to estimate the percentage contribution. It is, however, evident from the table that the contribution from 1p-3h and 3p-1h are negative and adds to the magnitude of ΔE . Whereas, the contribution from 2p-2h is positive and reduces the magnitude of ΔE .

4.4.2 Excitation energy of one-valence atoms

The ionization potentials and excitation energies calculated using coupledcluster CCSD method are presented in the Table. 4.3. In this case also we have chosen the same set of alkaline-earth ions as in the MBPT calculations. Comparison of these results with the experimental data can throw some light on the reliability of CCT. The largest deviations from the experimental data are 0.1% for state $D_{5/2}$ in Mg⁺, 2.5% for state $D_{5/2}$ in Ca⁺, 0.7% for state $P_{1/2}$ in Sr⁺ and 4.2% for state $D_{5/2}$ in Ba⁺. In the MBPT results, these are however 0.2% for $D_{3/2}$ in Mg⁺, 3.6% for $D_{5/2}$ in Ca⁺, 1.8% for $P_{1/2}$ in Sr⁺ and 9.9% for $D_{5/2}$ in Ba⁺. So the CCSD results are closer to the experimental data than the MPBT results. This is not surprising as CCSD encapsulates electron correlations more accurately.

Among the results from earlier works listed in the Table. 4.3, results of the Ref.[64], for Mg^+ , are obtained using the same method as ours. In addition, the correlation corrections due to the some dominant contributing triples cluster amplitudes and due to Breit interaction are also taken in to account. And therefore, as its evident from the table, the results of the Ref.[64] are more accurate than the ours. For other atomic systems, Ca⁺, Sr⁺ and Ba⁺, for most of the states our results are more accurate than the previous theoretical work Ref. [65]. This is perhaps expected as we have used more accurate method.

4.4.3 Magnetic dipole HFS constants

The magnetic dipole structure constants computed using coupled-cluster theory for the alkaline-earth ions are presented in the Table. 4.4. In all the ions considered, we have computed magnetic dipole HFS constants for the ground state $s_{1/2}$ and the few low lying excited states $p_{1/2}$, $p_{3/2}$, $d_{3/2}$ and $d_{5/2}$. For comparison, we also list the results from the other theoretical works and the experiments data. The respective contributions from the different terms in the

Ion	state	This v	work	Other	works	Exp.Ref[63].
		IP	EE	IP	EE	EE
$^{25}\mathrm{Mg^{+}}$	$3s_{1/2}$	-0.55203	0.0	-0.55252	0.0	0.0
	$3d_{3/2}$	-0.22666	0.32537	-0.22677	0.32575^{a}	0.32573
	$3d_{5/2}$	-0.22668	0.32535	-0.22677	$0.32575^{\rm a}$	0.32574
	$3p_{1/2}$	-0.38950	0.16253	-0.39003	0.16249^{a}	0.16252
	$3p_{3/2}$	-0.38917	0.16286	-0.38961	$0.16291^{\rm a}$	0.16294
$^{43}\mathrm{Ca}^+$	$4s_{1/2}$	-0.43671	0.0	-0.43836	0.0	0.0
	$3d_{3/2}$	-0.37601	0.06070	-0.37768	0.06068^{b}	0.06220
	$3d_{5/2}$	-0.37578	0.06093	-0.37731	0.06205^{b}	0.06247
	$4p_{1/2}$	-0.32128	0.11543	-0.32217	$0.11619^{\rm b}$	0.11478
	$4p_{3/2}$	-0.32119	0.11552	-0.32111	$0.11725^{\rm b}$	0.11580
$^{87}\mathrm{Sr}^+$	$5s_{1/2}$	-0.40573	0.0	-0.40839	0.0	0.0
	$4d_{3/2}$	-0.33926	0.06647	-0.34279	$0.06560^{ m b}$	0.06632
	$4d_{5/2}$	-0.33827	0.06746	-0.34132	$0.06707^{\rm b}$	0.06760
	$5p_{1/2}$	-0.29696	0.10877	-0.29838	$0.11001^{\rm b}$	0.10805
	$5p_{3/2}$	-0.29425	0.11148	-0.29463	0.11376^{b}	0.11171
$^{137}Ba^{+}$	$6s_{1/2}$	-0.36862	0.0	-0.37308	0.0	0.0
	$5d_{3/2}$	-0.34758	0.02104	-0.35172	0.02136^{b}	0.02221
	$5d_{5/2}$	-0.34386	0.02476	-0.34748	$0.02560^{\rm b}$	0.02586
	$6p_{1/2}$	-0.27483	0.09379	-0.27532	$0.09776^{\rm b}$	0.09232
	$6p_{3/2}$	-0.26821	0.10041	-0.26946	$0.10362^{\rm b}$	0.10002

Table 4.3: Ionization potentials and excitation energies using coupled-cluster theory for alkaline-earth ions. All values are in atomic units.

^a Reference[64]. ^b Reference[65].

state	This work	Other works	Experiment
		$^{25}{ m Mg^{+}}$	
$3s_{1/2}$	-596.785	$-597.6^{\rm l}, -554^{\rm s},$	
,		$-(602 \pm 8)^{t}$	$-596.254^{\rm m}$
$3p_{1/2}$	-102.997	$-103.4^{\rm l}, -100^{\rm s}$	-
$3p_{3/2}$	-19.546	$-19.29^{\rm l}, -19^{\rm s}$	-
$3d_{3/2}$	-1.083	$-1.140^{\rm l}, -1.25^{\rm s}$	-
$3d_{5/2}$	0.118	$0.1196^{\rm l}, 0.107^{\rm a}$	_
,		$^{40}\mathrm{Ca^{+}}$	
$4s_{1/2}$	-808.126	$-805.35^{\rm b}, -819^{\rm g},$	$-797.5(2.4)^{\rm c}$ $-805(2)^{\rm d}$
		$-794.7^{\rm h}, -806.4(2.5)^{\rm u}$	
$4p_{1/2}$	-142.782	$-143.07^{\rm b}, -148^{\rm g},$	$-158(3.3)^{\rm c}, -145.5(1.0)^{\rm d},$
		$-144.8^{\rm h}, -143^{\rm s},$	$-142(8)^{\rm e}, -145.4(0.1)^{\rm f}$
$4p_{3/2}$	-32.185	$-30.50^{\mathrm{b}}, -30.9^{\mathrm{g}},$	$-29.7(1.6)^{c}, -31.9(0.2)^{d},$
		$-29.3^{\rm h}, -30^{\rm s},$	$-31.0(0.2)^{\rm f}$
$3d_{3/2}$	-45.294	$-47.82^{\mathrm{b}}, -52^{\mathrm{g}},$	$-48.3(1.6)^{\rm e}, -47.3(0.2)^{\rm f}$
		$-49.4^{\rm h}, -47.3(3)^{\rm u}$	
$3d_{5/2}$	-4.008	$-3.351^{\mathrm{a}}, -3.55^{\mathrm{b}},$	$-3.8(0.6)^{\rm f}, 3.8931(2)^{\rm v}$
		$-5.2^{\mathrm{g}}, -4.2^{\mathrm{h}}, -3.6(3)^{\mathrm{u}}$	
		$^{87}\mathrm{Sr}^+$	
$5s_{1/2}$	-990.638	$-10003.18^{\rm b}, -1000^{\rm k}$	$-1000.5(1.0)^{i}$
$5p_{1/2}$	-169.988	$-178.40^{\rm b}, -177^{\rm k}, -175^{\rm s}$	-
$5p_{3/2}$	-36.225	$-35.11^{\rm b}, -35.3^{\rm k}, -30^{\rm s}$	-36.0^{i}
$4d_{3/2}$	-44.320	$-47.36^{\rm b}, -46.7^{\rm k}$	-
$4d_{5/2}$	2.168	$2.156^{\rm a}, 2.51^{\rm b}, 1.1^{\rm k}$	2.17^{j}
		$^{137}\mathrm{Ba^{+}}$	
$6s_{1/2}$	4021.721	4072.83^{p}	$4018.2^{\rm q}$
$6p_{1/2}$	705.039	736.98^{p}	-
$6p_{3/2}$	130.191	$130.94^{\rm p}, 126^{\rm s}$	$126.9^{\circ}, 112.77^{r}$
$5d_{3/2}$	185.013	$192.99^{\rm n}, 188.76^{\rm p}$ $215^{\rm o}$	$189.730^{\circ}, 170.88^{r}$
$5d_{5/2}$	-12.593	$9.39^{\rm n}, -11.717^{\rm a}, -18^{\rm o}$	-12.028°

Table 4.4: Magnetic dipole hyperfine structure constants (in MHz) for $^{25}{\rm Mg^+},$ $^{43}{\rm Ca^+},$ $^{87}{\rm Sr^+},$ and $^{137}{\rm Ba^+}$ ions.

^aReference[79].^bReference[80]. ^cReference[81]. ^dReference[82]. ^eReference[83]. ^fReference[84].^gReference[85]. ^hReference[86]. ⁱReference[87]. ^jReference[88]. ^kReference[89].^lReference[64]. ^mReference[90]. ⁿReference[91]. ^oReference[92]. ^pReference[93].^qReference[94]. ^rReference[95]. ^sReference[96]. ^tReference[97]. ^uReference[98].^vReference[99].

Table 4.5: Contributions from different terms in the coupled-cluster properties expression for magnetic dipole hyperfine constant. The values listed are in MHz.

State	Coupled-cluster terms								
	$\tilde{H}_{\rm hfs}$	$S^{\dagger} \tilde{H}_{\rm hfs}$	$S_2^{\dagger} \tilde{H}_{\rm hfs} S_1$	$S_1^{\dagger} \tilde{H}_{\rm hfs} S_1$	$S_2^{\dagger} \tilde{H}_{\rm hfs} S_2$	Norm			
		+c.c	+c.c.						
			$^{25}\mathrm{Mg^{+}}$						
$3s_{1/2}$	-479.433	-111.099	-1.637	-0.396	-5.560	1.002			
$3p_{1/2}$	-79.738	-21.951	-0.348	-0.089	-0.989	1.001			
$3p_{3/2}$	-15.937	-3.340	0.000	-0.018	-0.277	1.001			
$3d_{3/2}$	-1.266	0.186	0.004	-0.001	-0.008	1.001			
$3d_{5/2}$	543	0.648	0.017	-0.000	-0.004	1.001			
			$^{43}\mathrm{Ca}^+$						
$4s_{1/2}$	-601.783	-196.519	-4.782	-1.802	-10.717	1.009			
$4p_{1/2}$	-101.970	-39.042	-1.089	-0.446	-1.031	1.006			
$4p_{3/2}$	-19.969	-11.094	-0.244	-0.094	-1.004	1.007			
$\frac{3d_{3/2}}{3d_{3/2}}$	-36.107	-7.464	-0.128	-0.260	-2.153	1.018			
$3d_{5/2}$	-15.541	13.531	0.490	-0.111	-2.449	1.018			
- /									
			$^{87}\mathrm{Sr}^+$						
$5s_{1/2}$	-741.871	-235.962	-5.980	-3.046	-15.027	1.011			
$5p_{1/2}$	-123.038	-44.789	-1.199	-0.678	-1.446	1.007			
$5p_{3/2}$	-21.899	-13.096	-0.353	-0.126	-1.043	1.008			
$4d_{3/2}$	-34.452	-8.184	-0.263	-0.139	-1.979	1.016			
$4d_{5/2}$	-14.706	18.484	0.473	-0.058	-1.991	1.016			
			$^{137}Ba^{+}$						
$6s_{1/2}$	2964.012	1003.841	27.452	17.598	66.108	1.014			
$6p_{1/2}$	498.248	197.723	5.728	4.072	6.064	1.010			
$6p_{3/2}$	74.339	50.583	1.605	0.619	4.480	1.011			
$5d_{3/2}$	142.440	35.669	1.067	0.462	9.495	1.022			
$5d_{5/2}$	59.325	-80.381	-1.553	0.191	9.554	1.022			

Ion	state		S^{*}	${}^{\dagger} ilde{H}_{ m hfs}$	
		iter = 0	iter = 1	iter = 2	Converged
		$(H_{\rm hfs}e^T)_1$	$T_2^{\dagger}(H_{\rm hfs}e^T)_1T_2$	$T_2^{\dagger^2} (H_{\rm hfs} e^T)_1 T_2^2$	value
$^{25}\mathrm{Mg^{+}}$	$3s_{1/2}$	-53.663	-53.502	-53.503	-53.503
	$3p_{1/2}$	-10.627	-10.563	-10.564	-10.564
	$3p_{3/2}$	-1.592	-1.577	-1.577	-1.577
	$3d_{3/2}$	0.093	0.091	0.091	0.091
	$3d_{5/2}$	0.324	0.321	0.321	0.321
$43C_{0}+$	10.	00 100	80 776	80 778	80 778
Ua	$4s_{1/2}$	-90.109	-89.170	-09.110	-09.110
	$4p_{1/2}$	-10.757	-16.570	-10.074	-16.074
	$4p_{3/2}$	-4.845	-4.792	-4.793	-4.793
	$3d_{3/2}$	-3.851	-3.887	-3.885	-3.885
	$3d_{5/2}$	0.715	6.638	6.639	6.639
$^{87}\mathrm{Sr}^+$	$5s_{1/2}$	-109.153	-108.716	-108.720	-108.720
	$5p_{1/2}$	-22.116	-21.908	-21.912	-21.912
	$5p_{3/2}$	-6.006	-5.943	-5.944	-5.944
	$4d_{3/2}$	-4.216	-4.267	-4.265	-4.265
	$4d_{5/2}$	8.822	8.687	8.689	8.689
105					
$^{137}Ba^{+}$	$6s_{1/2}$	469.636	467.423	467.450	467.449
	$6p_{1/2}$	98.036	97.052	97.075	97.074
	$6p_{3/2}$	22.917	22.655	22.660	22.660
	$5d_{3/2}$	18.959	19.161	19.150	19.150
	$5d_{5/2}$	-36.806	-36.092	-36.104	-36.104

Table 4.6: Magnetic dipole hyperfine structure constant contributions from higher-order terms in the all order scheme.

couple-cluster hyperfine equation, Eq. (4.42), are given in the Table. 4.5. This table provides lot more information about the electron correlation arising from different terms. The second column, represented as $\tilde{H}_{\rm HFS}$, is the sum of the Dirac-Fock and the terms which have closed-shell cluster. Contribution from the later is found to be relatively much less than Dirac-Fock contribution.

In the case of Mg⁺ the experimental data is available only for the $3s {}^{2}S_{1/2}$ [90]. However, theoretical results are available for all the states. As evident from the table, our total value -596.78 for the state $3s {}^{2}S_{1/2}$ is in very good agreement with the experimental result, and is also consistent with the other theoretical results. The difference between our result and the experiment is about 0.08%. To compare results for the other states we resort on the other theoretical works. The results of the Safronova et. al [64] are obtained using linearized CCSD method which is similar to ours. In our case however nonlinear terms in the CC equation are also included. For the $3p {}^{2}P_{1/2}$ and $3p {}^{2}P_{3/2}$ states, our values -102.997 and -19.546 compares very well with the results of Ref. [64]. Our value of -1.083 for the state $3d^{2}D_{3/2}$ is larger, and 0.118 for the state $3d^{2}D_{5/2}$ is smaller than the Ref.[64]. As evident from the Table. 4.5, the largest contribution arise from the zeroth-order term. The second largest contribution is from $S^{\dagger}\tilde{H}_{\rm hfs} + c.c.$, this is expected as it has only one order of cluster amplitude.

The alkaline-earth ion Ca⁺ is well studied, experimentally and theoretically, and more data is available in the literature. It is evident from the Table. 4.4, there is a large variation in the experimental results of $4s \ ^2S_{1/2}$ and $4p \ ^2P_{1/2}$, and less in the results of $4p \ ^2P_{3/2}$, $3d \ ^2D_{3/2}$ and $3d \ ^2D_{5/2}$ states. The theoretical results, on the other hand, exhibit significant variations for all the states except 4p ${}^{2}P_{3/2}$. Our Dirac-Fock value -589.09 for the 4s ${}^{2}S_{1/2}$ is in good agreement with the previous theoretical results -589 [96] and -588.933 [80]. The small difference in DF value can be attributed to the nature of the basis functions used in the three calculations. Our total value -808.12 is marginally lower than the experimental values but lies between the other theoretical results. Similarly, for the states $4p \ ^2P_{1/2}$ and $4p \ ^2P_{3/2}$ our Dirac-Fock values of -101.47 and 19.65 are in excellent agreement with the other theoretical values -102 [96] and -101.492 [80], and -19.2 [96] and -19.646 [80], respectively. Our total value -142.782 for the state $4p \ ^2P_{1/2}$ is very close to the one of experimental results -142(8) of the Ref. [83], and is also in agreement with the theoretical results [80] and [96]. The total value -32.185 for the state $4p^2 P_{3/2}$ is smaller than all the previous theoretical values. However this is in good match with the experimental result -31.9(0.2) of Ref. [82]. Our total value -45.294 for the state $3d^{2}D_{3/2}$ is higher than the previous theoretical results and the experimental results. However the DF values -33.55 compares well with previous studies -33 [96] and -33.206 [80]. For the state $3d^{2}D_{5/2}$ our calculated value of -4.008 in very close to the experimental results in Refs. [84] and [99]. Our result is also in the range of the other theoretical results.

In the case of Sr^+ , the experimental data is available only for the states $5s {}^{2}S_{1/2}$, $5p {}^{2}P_{1/2}$ and $4d {}^{2}D_{5/2}$. However, there are several theoretical results in the literature. For the ground state, $5s^{2}S_{1/2}$, our total value is higher than both the theoretical and experimental results. The discrepancy is about 0.9% with respect to the experiment. Our DF value -738.204, is however, lower than the previous works -735 [89] and -736.547 [80]. The DF values from our work are -122.363 and -21.501 for the states $5p \,{}^2P_{1/2}$ and $5p \,{}^2P_{3/2}$ respectively. These are very close to the results from previous works, -122[89] and -121.576 [80] for the state $5p \,{}^2P_{1/2}$, and -21.4 [89] and -21.331 [80] for the state $5p {}^{2}P_{3/2}$. There is a large deviation, about 4%, in our result with respect to the other theoretical results for the state $5p^2P_{1/2}$. Our HFS total value for the state $5p \,{}^2P_{3/2}$ is in excellent agreement with the experiment. In fact our value is better than the previous results. There is no experimental data is available for the state $4d^2D_{3/2}$. Our value of -44.320 deviates from the other theoretical results [89] and [80]. The DF value -31.368 is however consistent with -31.2 [89] and -31.126 [80]. There is good agreement between our result 2.168, and the previous results 2.156 [79] and 2.51 [80] for the state $4d^{2}D_{5/2}$. The result of [79] is obtained with the same method and the basis functions as ours. Our result compares well also with the experimental value.

The theoretical study of Ba⁺ hyperfine constants is very important, as it is a potential candidate for the PNC experiments [100]. For the ground state $6s \, {}^2S_{1/2}$, the difference between our result and the experiment is small, $\sim 0.09\%$. The previous work of Ref. [93] uses the method and basis functions as ours. As noticeable in Table. 4.4, the difference between the two results is ~1.3%. Like in the ions considered earlier, the next to leading term is $S^{\dagger}H_{\rm hfs}$, it accounts for $\approx 23\%$ of the total value. The DF value of $6p \,{}^2P_{1/2}$ and $6p \,{}^2P_{3/2}$ in the previous work are 492.74 [93] and 71.84 [93]. These are different from our values of 504.196 and 73.674. The total result 705.039 for the state $6p \ ^2P_{1/2}$ is lower than the previous theoretical value 736.98 [79]. However, the total value of 130.191 for the state $6p \,{}^2P_{3/2}$ matches well with Ref. [79]. For the $5d \ ^2D_{3/2}$ state our value is slightly lower than the previous theoretical results. This is, however, lies within the range of the experimental data. The DF value of this state is closer to the Ref. [93]. For the 5d $^2D_{5/2}$ state, the total value -12.593 from the present work is better than the other theoretical works and the deviation from the experiment is about 4.5%.

We have also studied the HFS constants of Yb⁺. The magnetic dipole HFS constants are presented in the Table. 4.8. Unlike the alkaline-earth metal ions, there are very few theoretical results. Like Ba⁺, atomic Yb is also a promising candidate of atomic PNC experiments. Our results of the magnetic dipole HFS constant -3529.660 of the $6s \, {}^{2}S_{1/2}$ state is slightly lower than the experimental and other theoretical values, the difference is about 0.6%. The result of the Ref. [107] is better than ours. However, for the $6p \, {}^{2}p_{1/2}$ state our result is better than the Ref. [107], the corresponding differences are $\approx 2\%$ and $\approx 6\%$

respectively. For the $6p \ ^2p_{3/2}$, $5d \ ^2D_{3/2}$ and $5d \ ^2D_{5/2}$ states no experimental data is available. For the state $5d \ ^2D_{3/2}$ our result is consistent with the previous result of Ref. [91]. However, there is a large difference for the states $6p \ ^2p_{3/2}$ and $5d \ ^2D_{5/2}$. Our results are larger by $\approx 17\%$ and $\approx 536\%$ respectively for $6p \ ^2p_{3/2}$ and $5d \ ^2D_{5/2}$ than the previous results of Ref. [107] and Ref. [91].

4.4.4 All-order magnetic dipole HFS results

Table. 4.6 lists the results calculated from the iterative scheme to incorporate the higher-order terms in the dressed properties operator. As mentioned earlier, to test our scheme we implement it for the *loe* one of the effective operator. This contributes to the HFS constants through the term $S^{\dagger} \tilde{H}_{hfs}$. As it is listed in Table. 4.6, we start with the one order of cluster amplitude, the contribution from which is listed in the second column of the Table. 4.6. And then in each iteration we multiply by two orders of cluster amplitudes. For example, in the first iteration the new effective operator is third order in cluster amplitudes. We continue the interaction, until the difference of the HFS value converges. The converged values are listed in the last column of the table. After a detailed analysis we conclude that the contribution from the higher order, cubic and higher, terms are negligibly small. This is found to be less than 0.1% of the total value. And hence the terms with three or more orders of closed-shell cluster amplitude, in the dressed properties operator, can be neglected.

4.4.5 Electric quadrupole HFS constants

The electric quadrupole HFS constants calculated for the alkaline-earth ions are presented in the Table. 4.7. The same for the ion Yb⁺ is however listed in the Table. 4.8. For comparison, data from previous theoretical works as well as the experimental data are listed. In Table. 4.9 we provide the individual contributions from different terms in the coupled-cluster properties expression, Eq.(4.42). Like in magnetic dipole HFS constants, $\tilde{H}_{\rm HFS}$ is the sum of the contributions from the Dirac-Fock and the term which contribute through closed-shell cluster operators only. The individual contributions follow the same pattern as the magnetic dipole HFS constants. After the zeroth-order term, for all the ions, the dominant contribution is from $S^{\dagger}\tilde{H}_{\rm HFS}$, as it includes the core polarization effects.

To the best of our knowledge there are no experimental data on the quadrupole HFS constants for the $3p \ ^2p_{3/2}$, $3d \ ^2D_{3/2}$ and $3d \ ^2D_{5/2}$ states of Mg⁺. The theoretical results are also limited to the first two states. Our results 22.849 and 1.168 for the $3p \ ^2p_{3/2}$, $3d \ ^2D_{3/2}$ states respectively are very close to the results of the Ref. [101]. The better agreement in the two results is because of the same method, the coupled-cluster, employed.

Ion	state	This work	Other works	Experiment
$^{25}\mathrm{Mg^{+}}$	$3p_{3/2}$	22.849	$22.91^{\rm a}$	—
	$3d_{3/2}$	1.168	$1.26^{\rm a}$	_
	$3d_{5/2}$	1.673	_	_
	,			
$^{40}\mathrm{Ca^{+}}$	$4p_{3/2}$	-6.552	-6.505^{b}	$-6.7(1.4)^{\rm f}, -6.7(1.7)^{\rm g}$
	$3d_{3/2}$	-2.912	$-2.893^{\mathrm{b}}, -2.94^{\mathrm{c}},$	$-3.7(1.9)^{ m g}$
	,		$-2.777^{\rm d}, -2.77^{\rm e}$	
	$3d_{5/2}$	-4.301	$-4.107^{\mathrm{b}}, -4.18^{\mathrm{c}},$	$-3.9(6.0)^{\rm g}, -4.241(4)^{\rm h}$
	,		$-4.088^{\rm d}, -3.97^{\rm e}$	
$^{87}\mathrm{Sr^+}$	$5p_{3/2}$	84.806	$82.655^{i}, 83.662^{j}$	$88.5(5.4)^{l}$
	$4d_{3/2}$	33.961	$35.075^{\rm i}, 36.051^{\rm j},$	_
	,		39.60°	
	$4d_{5/2}$	48.055	$48.800^{\rm i}, 51.698^{\rm j},$	$49.11(6)^{m}$
	,		$56.451^{\rm c}$ $49.166^{\rm k}$	
$^{137}\mathrm{Ba^{+}}$	$6p_{3/2}$	98.954	92.275^{n}	$92.5(0.2)^{o}$
	$5d_{3/2}$	45.765	$51.32^{\rm c}, 47.3^{\rm p}, 46.82^{\rm n}$	$44.541(17)^{p}$
	$5d_{5/2}$	62.685	$68.16^{\circ}, 63.2^{p}, 62.27^{n}$	$59.533(43)^{\rm p}, 60.7(10)^{\rm q},$
	,			$62.5(40)^{ m r}$
	[404]	h D C		
^a Reference	ce[101].	^b Reference	[102]. ^c Reference[91].	^d Reference[80].
° Keterend	ce[85].	⁺ Keterence	[82]. ^g Keterence $[84]$.	" Keterence[99].
' Keterenc	e[89].	^J Reterence	[80]. $^{\kappa}$ Reference[79].	¹ Reterence[87].
" Referen	ce[88].	" Reference	[105]. ^o Reference $[106]$. ^p Reference[92].
^q Referen	ce[103].	^r Reference	[104].	

Table 4.7: The electric quadrupole HFS constant for ${}^{25}Mg^+$, ${}^{40}Ca^+$, ${}^{87}Sr^+$ and ${}^{137}Ba^+$ ions. All the values are in MHz.

Ion	state	This work	Other works	Experiment
		HFS constant a		
$^{173}\mathrm{Yb^{+}}$	$6s_{1/2}$	-3529.660	$-3507^{\rm a}$	$-3497.5(6)^{a}, -3508(9)^{c}$
	$6p_{1/2}$	-612.362	$-638^{\rm a}$	$-518.2(4)^{\mathrm{a}}, -600^{\mathrm{c}}$
	$6p_{3/2}$	-88.973	-107^{a}	—
	$5d_{3/2}$	-104.479	$-110.31^{\rm b}$	—
	$5d_{5/2}$	22.078	3.47^{b}	—
		HEC constant b		
172		nrs constant o		
1 ¹ 3 Yb ⁺	$6p_{3/2}$	1839.779	1780^{a}	$1460(50)^{a}$
	$5d_{3/2}$	902.301	$951.4^{\rm b}$	—
	$5d_{5/2}$	1165.046	$1190.4^{\rm b}$	—

Table 4.8: The magnetic dipole and electric quadrupole HFS constants for ¹⁷³Yb⁺. All the values are in MHz.

^a Reference[107]. ^b Reference[91]. ^c Reference[108]. ^d Reference[109].

Several theoretical and experimental data from the previous works implies that Ca⁺ is a well studied system. For all the states our calculated results are in good agreement with the other theoretical data. Our results -6.552 of the $4p \ ^2p_{3/2}$ state deviate from the experiment by about 2.2%. The deviation in the previous work of [102] is slightly larger than ours though both calculations employ the same method and single-electron basis functions. For the state $3d \ ^2D_{3/2}$, there are deviations in our as well as previous theoretical results from the experimental data. This requires further experimental investigations as only one data is available. For the $3d \ ^2D_{5/2}$ state there is excellent agreement with the experimental data, the difference is lower than $4p \ ^2p_{3/2}$.

Like Ca⁺, the electric quadrupole HFS constants of Sr⁺ has been studied in several theoretical works. Results from the other theoretical and experimental works along with the ours are listed in the Table. 4.7. Among the previous works, the calculations of Martensson [89] and Sahoo [79] uses the relativistic coupled-cluster. We also use the same method. However, the single electron basis functions used by Martensson [89] are different than ours and Sahoo [79]. As evident from the table, for all the states our results are lower than others. The present result 84.806 of $5p \, {}^2p_{3/2}$ state is marginally better than the other theoretical results. The result of Sahoo [79] for the $4d_{5/2}$ state is the best theoretical result in the table. It has less error with respect to the experiment.

Table 4.9	9: Electric	quadrupole	HFS	$\operatorname{constants}$	contributions	from	different
terms in	the coupled	l-cluster prop	pertie	s equation.			

State	e Coupled-cluster terms							
	$ ilde{H}_{ m hfs}$	$S^{\dagger} \tilde{H}_{\rm hfs} + c.c.$	$S_2^{\dagger} \tilde{H}_{\rm hfs} S_1 \\ + c.c.$	$S_1^{\dagger} \tilde{H}_{\rm hfs} S_1$	$S_2^{\dagger} \tilde{H}_{\rm hfs} S_2$	Other terms	Norm	
			25Mg+					
$6n_{2/2}$	164 484	109 511	4 024	2.565	7769	-2.302	1 001	
$5d_{2/2}$	88 818	26 888	-573	1.073	-3.540	-0.791	1.001	
$5d_{5/2}$	126.565	34.180	848	1.377	-1.911	-1.081	1.005	
			$^{40}\mathrm{Ca^{+}}$					
$6p_{3/2}$	223.341	170.985	7.425	5.364	-1.153	-3.097	1.002	
$5d_{3/2}$	147.733	46.886	.211	1.305	-7.849	-1.213	1.006	
$5d_{5/2}$	198.596	63.015	.333	1.627	-5.898	-1.508	1.005	
			$^{87}\mathrm{Sr}^+$					
$6p_{3/2}$	164.484	109.511	4.024	2.565	7.769	-2.302	1.001	
$5d_{3/2}$	88.818	26.888	573	1.073	-3.540	-0.791	1.005	
$5d_{5/2}$	126.565	34.180	848	1.377	-1.911	-1.081	1.005	
			137 D . +					
C	000 941	170.005		F 904	1 159	2 007	1 000	
$5p_{3/2}$	223.341	170.985	(.425	5.304	-1.153	-3.097	1.002	
$5a_{3/2}$	147.733	40.880	.211	1.305	-7.849	-1.213	1.000	
$5d_{5/2}$	198.596	63.015	.333	1.627	-5.898	-1.508	1.005	
			173Yb ⁺					
$6p_{3/2}$	56.039	274.025	11.547	9.994	-0.212	6.441	1.001	
$5d_{3/2}$	210.175	112.382	1.292	3.058	-4.128	0.975	1.005	
$5d_{5/2}$	255.658	152.106	2.217	3.080	4.774	-0.041	1.004	

Ours on the other hand is $\approx 2.3\%$ lower than his result.

In the case of Ba⁺, result of Sahoo [105] for state the $6p \ ^2p_{3/2}$ compares very well with experimental data. Our results for the same is about 7% larger than his result. However, a remarkably good agreement is found between our results and the experiment for $5d_{3/2}$ and $5d_{5/2}$ states. Our result 62.685 for the $5d_{5/2}$ state is consistent with the value 62.27 in Sahoo [105]. This is expected, as mentioned earlier, both calculations employ the same many-body method. However, for the state $5d_{3/2}$ our result is closer to the experimental data than that of the Ref. [105]. This difference in the results could be on account of minor differences in the exponents used in the basis set generation or the truncation of the coupled-cluster properties expression.

The electric quadrupole HFS constant for Yb⁺ has not been studied in fine detail. As evident from the Table. 4.8, experimental data is available only for $6p \ ^2p_{3/2}$ state. A large deviation is observed for this state. The error is about 26% and 22% respectively in our value and the result of the Martensson and collaborators [107]. Our results are lower but close to the values from Itano [91]. A closer inspection of the results from Itano's calculations of the other ions (Sr⁺ and Ba⁺) reveals that, his results are consistently higher than the other theoretical and experimental data. One possible reason could be the contracted nature of the virtual orbitals, referred to as the correlation orbitals, in MCDF calculations. Hence we can expect a similar trend in Yb⁺ as well and it is possible that our results may be closer to the actual values.

4.4.6 Electric dipole transition amplitudes

Like in HFS constants, we use CC wave functions and calculate the reduced matrix element of the dipole operator **D** for the alkaline-earth ions Sr^+ and Ba^+ , and Yb^+ . Results from our calculations are listed in Table. 4.10 and the contributions from different terms in the properties expression are given in Table. 4.11. It is evident from this table, like the HFS constants, in all the ions considered the dominant contribution arises from the DF term. The second largest contribution is from the term with one order in the open-shell cluster amplitude. As listed in the penultimate column of the table, the contribution from the $S_2^{\dagger}\tilde{D}S_2$ is larger than $S_1^{\dagger}\tilde{D}S_2$ or $S_2^{\dagger}\tilde{D}S_1$. This is because of the fact that S_2 are in general larger than S_1 .

Our Dirac-Fock value of the E1 transition amplitudes matches well with the results of Guet and Johnson [65] for Sr⁺ and Ba⁺. The total value from our calculations are however higher for Sr⁺. The difference could be largely attributed to the higher order core-polarization effects associated with the random-phase approximation (RPA). The RPA effects are incorporated in the coupled-cluster but not to higher order as in an iterative RPA calculations.

Unlike Sr^+ and Yb^+ there are several theoretical calculations of E1 transition matrix elements for Ba^+ . Among the previous works, the results of Sahoo

Ion	Transition	This work	Other works
$^{87}\mathrm{Sr}^+$	$5p_{1/2} \longrightarrow 5s_{1/2}$	3.2180	3.060^{a}
	$5p_{3/2} \longrightarrow 5s_{1/2}$	4.9223	4.325^{a}
	$5p_{1/2} \longrightarrow 4d_{3/2}$	3.4315	3.052^{a}
	$5p_{3/2} \longrightarrow 4d_{3/2}$	1.4217	1.355^{a}
	$5p_{3/2} \longrightarrow 4d_{5/2}$	4.5942	4.109^{a}
$^{137}\mathrm{Ba^{+}}$	$6p_{1/2} \longrightarrow 6s_{1/2}$	3.1974	$3.300^{\rm a}, 3.36(1)^{\rm b}, 3.272^{\rm c}$
	$6p_{3/2} \longrightarrow 6s_{1/2}$	5.0330	$4.658^{\rm a}, 4.73(3)^{\rm b}, 4.614^{\rm c}$
	$6p_{1/2} \longrightarrow 5d_{3/2}$	3.0898	$3.009^{\rm a}, 3.11(3)^{\rm b}, 3.008^{\rm c}$
	$6p_{3/2} \longrightarrow 5d_{3/2}$	1.2448	$1.312^{\rm a}, 1.34(2)^{\rm b}, 1.313^{\rm c}$
	$6p_{3/2} \longrightarrow 5d_{5/2}$	4.1347	$4.057^{\rm a}, 4.02(7)^{\rm b}, 4.054^{\rm c}$
$^{173}{\rm Yb^{+}}$	$6p_{1/2} \longrightarrow 6s_{1/2}$	2.9069	2.731^{d}
	$6p_{3/2} \longrightarrow 6s_{1/2}$	4.5256	3.845^{d}
	$6p_{1/2} \longrightarrow 5d_{3/2}$	3.6317	3.782^{d}
	$6p_{3/2} \longrightarrow 5d_{3/2}$	1.4918	1.546^{d}
	$6p_{3/2} \longrightarrow 5d_{5/2}$	4.8500	4.769^{d}

Table 4.10: Magnitude of the electric dipole transition amplitudes for $^{87}{\rm Sr^+},$ $^{137}{\rm Ba^+},$ and $^{173}{\rm Yb^+}$ ions.

^a Reference[65]. ^b Reference[98]. ^c Reference[110]. ^d Reference[111].

Transition		(Coupled-clus	ster terms		
	\tilde{D}	$S^{\dagger}\tilde{D}$	$S_2^{\dagger} \tilde{D} S_1$	$S_1^{\dagger} \tilde{D} S_1$	$S_2^{\dagger} \tilde{D} S_2$	Norm
			+c.c.	+c.c.		
			$^{87}\mathrm{Sr}^+$			
$5p_{1/2} \to 5s_{1/2}$	3.4877	-0.2715	-0.0043	0.0129	0.0233	0.9909
$5p_{3/2} \rightarrow 5s_{1/2}$	4.9265	-0.0072	-0.0003.1	0.0187	0.0034	0.9902
$5p_{1/2} \rightarrow 4d_{3/2}$	3.7250	0.2902	-0.0062	0.0178	0.0234	0.9889
$5p_{3/2} \rightarrow 4d_{3/2}$	1.6544	-0.2332	-0.0028	0.0080	0.0122	0.9882
$5p_{3/2} \rightarrow 4d_{5/2}$	-4.9942	0.3967	0.0085	-0.0238	-0.0334	0.9887
			$^{137}\mathrm{Ba^{+}}$			
$6p_{1/2} \rightarrow 6s_{1/2}$	3.8930	-0.7618	-0.0097	0.0442	0.0715	0.9880
$6p_{3/2} \to 6s_{1/2}$	-5.4824	0.5275	0.0134	-0.0609	-0.0973	0.9872
$6p_{1/2} \rightarrow 5d_{3/2}$	-3.7530	0.7220	-0.0001	-0.0392	-0.0685	0.9846
$6p_{3/2} \rightarrow 5d_{3/2}$	1.6471	-0.4240	0.0005	0.0161	0.0363	0.9838
$6p_{3/2} \rightarrow 5d_{5/2}$	5.0107	-0.9544	0.0011	0.0485	0.0930	0.9847
			$^{173}\mathrm{Yb^{+}}$			
$6p_{1/2} \to 6s_{1/2}$	3.2433	-0.3387	-0.0071	0.0181	0.0247	0.9872
$6p_{3/2} \to 6s_{1/2}$	-4.5458	0.0282	-0.0001	-0.0231	-0.0430	0.9868
$6p_{1/2} \to 5d_{3/2}$	-3.8635	0.2336	0.0095	-0.0286	-0.0366	0.9869
$6p_{3/2} \rightarrow 5d_{3/2}$	0.6972	-0.2551	-0.0039	0.0114	0.0165	0.9865
$6p_{3/2} \to 5d_{5/2}$	-5.1994	0.3448	0.0117	-0.0325	-0.0443	0.9881

Table 4.11: The electric dipole transition amplitude, contributions from different terms in the coupled-cluster theory.

and collaborators [98] are obtained using the same many-body method as ours. The single-electron basis functions are also same as we have used in the current calculations. In the other work [110], they employed the sum over state scheme in which correlation effects are selectively incorporated from the dominant contributing states. This scheme is in general less accurate than ours. Except the $6p_{3/2} \rightarrow 5d_{3/2}$ and $6p_{3/2} \rightarrow 5d_{5/2}$ transitions, an interesting pattern is observed for the first three transitions. Our results are higher than [110] but lies below of [98]. For the transitions $6p_{3/2} \rightarrow 5d_{3/2} \oplus 5d_{5/2}$, however, our results are lower and higher respectively than the other two results.

For Yb⁺, the work of Safronova and Safronova [111] is the only previous study on the electric dipole matrix elements. Their calculations are based on the third order relativistic MBPT and the excellent agreement between the length and velocity gauge results indicates the results are quite accurate. Except the $6p_{3/2} \rightarrow 6s_{1/2}$ transition, our results compare reasonably well with the Ref. [111]. For the $6p_{3/2} \rightarrow 6s_{1/2}$ transition, however, a larger deviation is observed. Our result is about 18% larger than the result of Ref. [111].

Chapter 5

Coupled-cluster theory of two-valence atoms

Apart from the atomic physics CCT has been extensively employed with great success to study other many-body systems. In the context of atoms, the single valence CCT has been applied to a large number of systems for *ab initio* calculations of properties [71, 72, 112, 26, 98, 113]. However, for two-valence systems there are very few attempts to implement CCT and these are limited to wave-function calculations [114, 115]. The reason is, the two-valence CCT, unlike the closed-shell and one-valence atoms, is nontrivial. There are three factors which contributes to the complexity of two-valence CCT. First, though the many-particle states (determinantal states) spanning the model space are well defined, the model functions are not defined. For this diagonalization of the effective Hamiltonian required. Second, atomic states are eigen states of the total angular momentum obtained from coupling the angular momenta of the two valence electrons. This leads to complication in the angular factors associated with the antisymmetrised many electron wave functions. And finally, calculations often diverges because of the *intruder* states. In subsequent sections, we discuss these points in some details and illustrate ways to overcome these difficulties.

This chapter is broadly separated in to four sections. Sec. I provides an overview of the multi-reference coupled-cluster with respect to the singlereference case. The *complete* and incomplete model spaces are then defined. The divergence of the CC equations arising from the *intruder* states are also discussed in the same section. The two-valence CC equations are derived in the Sec. II. The schemes for properties calculations of the two-valence atoms are illustrated in the Sec. III. And finally, the results are presented and analyzed in the last section of the chapter.



Chapter 5. Coupled-cluster theory of two-valence atoms

Figure 5.1: Energy level diagrams for the open-shell two-valence atoms.

5.1 Overview of multi-reference CCT

The multi-reference coupled-cluster (MRCC) is important in the study of the systems which are degenerate. In multi-reference theory, unlike the single reference case, several determinants span the model space. Within the frame work of CCT, there are two approaches to multi-reference theory. These are the

- Hilbert-space MRCC or the state-universal MRCC (SU-MRCC) and
- Fock-space MRCC or the valence-universal MRCC (VU-MRCC).

In the state universal MRCC approach [116, 117, 118, 119, 120] the wave operator is unique defined for each of the reference states. In other words, the wave operator is state dependent. That is

$$\Omega = \sum_{i} \Omega_i = \sum_{i} e^{S^i} P_i, \qquad (5.1)$$

where P_i is the projection operator expressed in terms of the determinants which are the part of model space. The summation index *i* runs over the all determinants. *S* is the excitation operator refereed to as the cluster operator.

In the valence-universal MRCC [121, 122, 123, 124, 125] the wave-operator is common to all the states. The wave operator in this approach is therefore expressed as

$$\Omega = \{e^S\}P.\tag{5.2}$$

The detailed discussions on valence-universal CCT and subtle issues related to the choice of model spaces are given in the review paper of Lindgren and Mukherjee [117]. In the present study, we implement the valence-universal MRCC within the frame work of an all particle approach. The theory can however be extended to systems with both particles and holes. In the all particle approach, the valence electrons are treated as particles [126] and each sector- closed-shell, one-valence and two-valence-are separate Hilbert spaces.

5.1.1 Complete model space

As mentioned in the previous section, for multi-reference systems a model space may consist of several configurations with the valence electrons assigned in different ways. The model space is complete if it includes all the possible configurations. To illustrate, consider the example of the low lying valence states 6s, 6p and 5d in atomic Yb. From these states the two-valence configurations, formed by arranging two electrons in all possible ways, are 6s6p, 5d6s, 5d6p, $6s^2$, $6p^2$ and $5d^2$. A complete model space incorporates all of these configurations.

The key advantage of choosing complete model space (CMS) is that the wave operator linked. This is because the excitation operators x_{\dots}^{\dots} are common to all the determinants in the model space. And consequently, x_{\dots}^{\dots} uniquely separates into internal and external sectors. The external excitations are cluster operators which excite electrons from cores to valence, valence to virtuals and cores to virtuals. The internal excitations are those which involve only valence orbitals. In other words, external excitations contribute to Ω and projects a model function to the complementary space. Whereas, internal excitations connect one model function to another model function and occurs in the definition of H_{eff} . Such a neat separation of the excitations is specific to CMS and another class of model space referred to as quasicomplete [127]. However, the Hilbert spaces of two-valence subsumes the one-valence after a direct product with a spectator valence state and similarly the closed-shell after direct product with two valence states.

5.1.1.1 Intruder states

In the case of CMS, specially when it is large, it is very likely that the energy range of the model space and the complementary space overlaps. When it does overlap, states of the orthogonal space which have energies within the range of the model space are referred to as the *intruder* states. Salomonson and collaborators were the first to encounter the convergence difficulty because of the intruder states in the atomic Be [128]. In the CCT the *intruder* state leads to difficulties in obtaining the converged solutions of the nonlinear CC equations. This is because, the equations are solved iteratively and divergences occur when the denominators are small. This the main drawback of working with the CMS in CCT.

Consider again the example of the low-lying levels of Yb atom. The first few excited states important in precision spectroscopy are $6s^2$ (¹S₀), 6s6p (³P_J),

 $5d6s ({}^{3}D_{j})$ and $6s6p ({}^{1}P_{1})$. The 6s, 6p and 5d are the obvious choice of valence shells. As mentioned earlier, CMS of the system then consists of the configurations: $6s^{2}$, 6s6p, 5d6s, 5d6p, $6p^{2}$ and $5d^{2}$ and all the other configurations are in the complementary space. As shown in Fig. 5.2, the levels from the orthogonal space $6p7p ({}^{3}P_{J})$, $6s7s ({}^{3}S_{1})$ and $6s7s ({}^{1}S_{0})$ lie within the model space. With several orthogonal functions within the energy domain of model functions, CMS based CCT calculations of Yb are likely to face with intruder state related divergences. Indeed, we do encounter divergence while working with CMS not only for Yb but in the other two-valence atoms (Ca, Sr and Ba) as well.



Figure 5.2: Low-lying energy levels of atomic Yb. This diagram shows the occurrence of the intruder states in atomic Yb.

5.1.2 Incomplete model space

one method to mitigate the divergence arising from *intruder* states is to work with the smaller model space referred to as the incomplete model space. In these model spaces, only selected the all valence configurations span the model space and remaining are part of the complementary space. There are however disadvantages of working with an incomplete model space. First, the clean separation of internal and external cluster amplitudes is no longer true. And second, the subsystem embedding condition is violated. For example, cluster operators which are external in one-valence Hilbert space may no longer be so in the two-valence Hilbert space. However, all the good virtues of CMS, in the context of Fock-space CCT, are applicable when the model space is quasicomplete. For a lucid description of what constitutes a quasicomplete model space refer [117, 127].

To provide an example of IMS consider again the low-lying states of Yb. An ideal incomplete model space would consist of the configurations $6s^2$, 6s6p and 5d6s. Model space would then encompass all the levels important to ongoing precision experiments: $6s^2$ (${}^{1}S_0$), 6s6p (${}^{3}P_J$), 5d6s (${}^{3}D_j$) and 6s6p (${}^{1}P_1$). The advantage of such a selection of model space is the separation, as evident in Fig. 5.2, from the potential *intruder* states 6p7p (${}^{3}P_J$), 6s7s (${}^{3}S_1$) and 6s7s (${}^{1}S_0$). Here, we can apply subduction process to check if the model space considered is quasicomplete and is shown in Fig. 5.3.



Figure 5.3: Incomplete model space of Yb two-valence calculations. Arrows indicate the *subduction* to lower valence sectors and respective model spaces.

As depicted in the Fig. 5.3, the initial stage is the two valence model space consisting of the two electron configurations $6s^2$, 6s6p and 5d6s. Removal of one electron from each of the configurations lead to a configuration in onevalence model space, 6s, 6p and 5d. And finally, removal of another electron gives the closed-shell model space, a determinantal state of the core orbitals. All the configurations obtained in the subduction are part of respective model spaces. This is the requirement of quasicomplete model space and necessary condition for separation of internal and external excitations.

5.2 Coupled-cluster equations

5.2.1 Exponential ansatz

The eigen value equation of the two-valence systems to solved with coupledcluster theory is

$$H^{\rm DC}|\Psi_{vw}\rangle = E_{vw}|\Psi_{vw}\rangle. \tag{5.3}$$

 $|\Psi_{vw}\rangle$ and E_{vw} are the exact function and the energy respectively. The indices v and w, here, represent the valence orbitals. In the coupled-cluster

$$|\Psi_{vw}\rangle = e^T \left[1 + S_1^{(1)} + \frac{1}{2}S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right] |\Phi_{vw}\rangle.$$
 (5.4)

Where, T is the cluster operator of the closed-shell part of the two-valence system. In CCSD approximation $T = T_1 + T_2$ and are solutions of, as described in the previous chapter, the Eqs. (4.8) and (4.9). $S_1^{(1)}$ and $S_2^{(1)}$ are the onevalence cluster operators of the two-valence system and these are the solutions of the Eqs. (4.31) and (4.32)respectively. The two-valence cluster operator $S^{(2)}$, in Eq.(5.4) has only double $S_2^{(2)}$ as it operates on the two-valence reference state. Like the closed-shell case and one-valence systems, $|\Phi_{vw}\rangle$ is the Dirac-Fock reference state of the two-valence system.



Figure 5.4: Representation of the cluster operators which contribute to the coupled-cluster equations for two-valence atoms.

Using the form of the wave function $|\Psi_{vw}\rangle$ from Eq. (5.4) in Eq. (5.3) and operating with e^{-T} , we get

$$e^{-T}He^{T}\left[1+S_{1}^{(1)}+\frac{1}{2}S_{1}^{(1)^{2}}+S_{2}^{(1)}+S_{2}^{(2)}\right]|\Phi_{vw}\rangle = E_{vw}\left[1+S_{1}^{(1)}+\frac{1}{2}S_{1}^{(1)^{2}}+S_{2}^{(1)}+S_{2}^{(2)}\right]|\Phi_{vw}\rangle.$$
(5.5)

Using the normal-ordered form the Hamiltonian, $H = H_{\rm N} + E_{vw}^{\rm DF}$, we can further write

$$\overline{H}_{N} \left[1 + S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right] |\Phi_{vw}\rangle = \Delta E_{vw}^{corr} \left[1 + S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right] |\Phi_{vw}\rangle,$$
(5.6)

where $\Delta E_{vw}^{\text{corr}}$, $= E_{vw} - E_{vw}^{\text{DF}}$, is the correlation energy of the two-valence atoms. As evident from Eq. (5.6), expression of the correlation energy is obtained by projecting with the reference state $\langle \Phi_{vw} \rangle$, in the form

$$\langle \Phi_{vw} | \overline{H}_{N} \Big[1 + S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \Big] | \Phi_{vw} \rangle = \Delta E_{vw}^{\text{corr}}.$$
 (5.7)

In deriving Eq.(5.7) we have used the relations $\langle \Phi_{vw} | S_2^{(1)} + \frac{1}{2} S_1^{(1)^2} | \Phi_{vw} \rangle = 0$, and $\langle \Phi_{vw} | S_2^{(2)} | \Phi_{vw} \rangle = 0$, since operation of $S^{(1)}$ and $S^{(2)}$ on $| \Phi_{vw} \rangle$ produce states orthogonal to $| \Phi_{vw} \rangle$.

To derive the coupled-cluster equations project Eq. (5.6) on the doubly excited determinant $\langle \Phi_{vw}^{pq} |$. We then get

$$\langle \Phi_{vw}^{pq} | \overline{H}_{N} \Big[1 + S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \Big] | \Phi_{vw} \rangle = \Delta E_{vw}^{corr} \langle \Phi_{vw}^{pq} | \Big[S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \Big] | \Phi_{vw} \rangle,$$
 (5.8)

This is the two-valence coupled-cluster equation. As evident from the equation, to calculate $S_2^{(2)}$ we need the cluster operators T_1 , T_2 , $S_1^{(1)}$, and $S_2^{(1)}$. Using Wick's theorem Eq. (5.8) can be reduced to the form

$$\langle \Phi_{vw}^{pq} | \bar{H}_{N} + \{ \bar{H}_{N} S_{1}^{(1)} \} + \{ \bar{H}_{N} S_{2}^{(1)} \} + \{ \bar{H}_{N} S_{2}^{(2)} \} + \frac{1}{2} \{ \bar{H}_{N} S_{1}^{(1)^{2}} \} | \Phi_{vw} \rangle =$$

$$E_{vw}^{\text{att}} \langle \Phi_{vw}^{pq} | \left[S_{1}^{(1)} + S_{2}^{(1)} + S_{2}^{(2)} + \frac{1}{2} S_{1}^{(1)^{2}} \right] | \Phi_{vw} \rangle.$$
(5.9)

 E_{vw}^{att} is the difference of the correlated energy of the (n-2)-electron (closedshell) atoms from that of *n*-electron (two-valence) atoms. It is referred to as the two-electron attachment energy. Later we describe the diagrams contributing to E_{vw}^{att} and also the procedure to calculate the excitation energy.

5.2.2 Generalized Bloch equation

So far, the CC equations were derived from the eigenvalue equation of the Dirac-Coulomb Hamiltonian. In this section we discuss an alternative approach to derive the two-valence CC equations. It is based on the generalized Bloch equation and this approach is more transparent implementing the CC equations with incomplete model space. For further consideration, take the generalized Bloch equation, Eq. (2.26), the renormalization term on the right hand side is often defined as

$$W = PV\Omega P = (V\Omega)_{\text{close}}.$$
(5.10)

Here, *close* indicates that the operator W acts only within the model space. Diagrammatically, the operator has no free lines in the closed-shell sector and only valence orbitals as free lines in the open-shell sector. Using Eq. (5.10), we can write Eq. (2.26) as

$$[\Omega, H_0]P = (V\Omega - \Omega W)P.$$
(5.11)
From the CC wave function given in Eq. (5.4), the above equation reduces to

$$\left[e^{T}\left(1+S_{1}^{(1)}+\frac{1}{2}S_{1}^{(1)^{2}}+S_{2}^{(1)}+S_{2}^{(2)}\right),H_{0}\right]|\Phi_{vw}\rangle = \left[Ve^{T}\left(1+S_{1}^{(1)}+\frac{1}{2}S_{1}^{(1)^{2}}+S_{2}^{(1)}+S_{2}^{(1)}+S_{2}^{(2)}\right)W\right]|\Phi_{vw}\rangle.$$
 (5.12)

In the right-hand side of Eq. (5.12), we can write

$$Ve^{T} = \left(V + \{VT\} + \frac{1}{2!}\{VTT\} + \frac{1}{3!}\{VTTT\} + \frac{1}{4!}\{VTTTT\}\right)e^{T},$$

= $(Ve^{T})_{\text{conn}}e^{T} = \bar{V}e^{T}.$ (5.13)

More details of the derivation are given in Ref. [126]. Using Eq. (5.13) in Eq. (5.12) and removing e^T from both sides of the equation we then get

$$\left[\left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right), H_0 \right] |\Phi_{vw}\rangle = \left[\bar{V} \left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(1)} + S_2^{(2)} \right) - \left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right) W \right] |\Phi_{vw}\rangle.$$
(5.14)

The CC equation is obtained by projecting this equation with the doubly excited determinant $\langle \Phi_{vw} |$. And then it is further simplified using Wick's theorem. As as consequence, there are connected and disconnected terms. However, only the connected terms contribute [47] to Eq. (5.14) and we can write

$$\langle \Phi_{vw}^{pq} | \left[\left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right), H_0 \right]_{\text{conn}} | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} | \left[\bar{V} \left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right) - \left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right) W \right]_{\text{conn}} | \Phi_{vw} \rangle,$$

$$(5.15)$$

where the subscript *conn* refers to connected terms. This equation can be considered as the CC equation of the two-valence system derived from the generalized Bloch equation. This, however, can further be simplified through explicit representation of the contractions. Consider the left hand side of the Eq. (5.15), we can simplify it as

$$\langle \Phi_{vw}^{pq} | \left[\left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right), H_0 \right]_{\text{conn}} | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} | \left\{ (1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) H_0 \right\} - \left\{ H_0(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) \right\} | \Phi_{vw} \rangle.$$

$$(5.16)$$

Similarly the terms on right hand side of the Eq. (5.15) are

$$\begin{split} \langle \Phi_{vw}^{pq} | \left[\bar{V} \left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right) \right]_{\text{conn}} | \Phi_{vw} \rangle = \\ \langle \Phi_{vw}^{pq} | \{ \overline{V(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) \} | \Phi_{vw} \rangle, \end{split}$$

and

$$\langle \Phi_{vw}^{pq} | \left[\left(1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right) W \right]_{\text{conn}} | \Phi_{vw} \rangle = \left[\langle \Phi_{vw}^{pq} | \{ (S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) W \} | \Phi_{vw} \rangle, \quad (5.17)$$

since the operator W acts only within the P space $\langle \Phi_{vw}^{pq} | W | \Phi_{vw} \rangle = 0$. From the definition of the normal Hamiltonian $\bar{H}_{\rm N} = \bar{V} + \bar{H}_0$ and hence, we can combine two of the terms as

$$\langle \Phi_{vw}^{pq} | \{ H_0(1 + S_1^{(1)} + \frac{1}{2}S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) \} + \\ \{ \overline{V(1 + S_1^{(1)} + \frac{1}{2}S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) } | \Phi_{vw} \rangle = \\ \langle \Phi_{vw}^{pq} | \{ \overline{H_N(1 + S_1^{(1)} + \frac{1}{2}S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}) } | \Phi_{vw} \rangle.$$
(5.18)

Using Eqs. (5.16), (5.17) and (5.17) in (5.15), and define the effective Hamiltonian as $H_{\text{eff}} = H_0 + W$, we get the CC equation as

$$\langle \Phi_{vw}^{pq} | \{ \overline{H_N(1+S_1^{(1)}+\frac{1}{2}S_1^{(1)^2}+S_2^{(1)}+S_2^{(2)})} \} - \\ \{ (S_1^{(1)}+\frac{1}{2}S_1^{(1)^2}+\overline{S_2^{(1)}+S_2^{(2)}}) H_{\text{eff}} \} | \Phi_{vw} \rangle = 0.$$
 (5.19)

The effective Hamiltonian, in above equation, acts within the model space only and hence the contributing diagrams are close in nature. The above equation can therefore also be written as

$$\langle \Phi_{vw}^{pq} | \{ \overline{H_N(1+S_1^{(1)}+\frac{1}{2}S_1^{(1)^2}+S_2^{(1)}+S_2^{(2)})} \} | \Phi_{vw} \rangle = H_{\text{eff}} \langle \Phi_{vw}^{pq} | (S_1^{(1)}+\frac{1}{2}S_1^{(1)^2}+S_2^{(1)}+S_2^{(2)}) | \Phi_{vw} \rangle.$$
 (5.20)

This is identical to Eq. (5.9), which is obtained from the eigen value equation of the Dirac-Coulomb Hamiltonian with the exponential ansatz.

5.2.3 Renormalization term in the open-shell CCT

The nonzero renormalization term in the CC equation is the predominant departure of open-shell CC equation from closed-shell CC. In the context of MBPT it arises in the contraction of the wave operator with the close term $PV\Omega P$. In CCT too it arises from the contraction of the cluster operator with the energy term. In the closed-shell case, Eqs. (4.8) and (4.9), renormalization term vanishes as the energy diagrams do not have any free lines and cannot contract with the cluster operator. For the open-shell case, energy diagrams have incoming and outgoing valence free lines and these can contract with the cluster diagram of S. This leads to nonzero renormalization term.

For example consider the case of two-valence CC, Eq. (5.9). In MBPT, the diagrammatic representation of the renormalization terms require a contortion to obtain correct energy denominators. Though CCT is a non-perturbative theory and energy denominators do not arise, we adopt the same convention to represent renormalization terms. So that these are distinct from the normal terms. As example, the folded diagrams which contribute to the renormalization term in two-valence CCT are shown in the Fig. 5.5.



Figure 5.5: Folded diagrams from the renormalization term in the generalized Bloch equation of two-valence systems. In two-valence coupled-cluster theory these diagrams arise from (a) $E_{vw}^{\text{att}} \langle \Phi_{vw}^{pq} | S_2^{(1)} | \Psi_{vw} \rangle$, (b) $E_{vw}^{\text{att}} \langle \Phi_{vw}^{pq} | S_1^{(1)} | \Psi_{vw} \rangle$ and (c) $E_{vw}^{\text{att}} \langle \Phi_{vw}^{pq} | S_2^{(2)} | \Psi_{vw} \rangle$.

5.3 **Properties calculations**

In this section we describe the schemes to calculate properties with the CC wave functions of the two-valence systems. Unlike the case of closed-shell and one-valence atoms, it is nontrivial for systems with more than one valence electrons. We first describe method to calculate the ionization potential and excitation energy, then the procedure for the HFS constants calculation is illustrated and finally, the calculation of E1 transition amplitude.

5.3.1 Excitation energy from CCT

The two-electron attachment energy in Eq. (5.9), is also expressed as

$$E_{vw}^{\text{att}} = \epsilon_v + \epsilon_w + \Delta E_{vw}^{\text{att}}, \qquad (5.21)$$

where, ϵ_v and ϵ_w are the Dirac-Fock energy of the valence orbitals. And $\Delta E_{vw}^{\text{att}} = \Delta E_{vw}^{\text{corr}} - \Delta E_0^{\text{corr}}$, is the difference between the correlation energies of closed-shell and two-valence sector of the atom. $\Delta E_{vw}^{\text{att}}$ in Eq. (5.21) is represented by the closed diagrams with free lines representing the valence states at the vertices's. Diagrams contributing to $\Delta E_{vw}^{\text{att}}$ can be separated in to one- and two-body types. The one-body diagrams are similar to those in Fig. (2.4) but with the bottom interaction (dotted line) replaced by cluster amplitude (solid line). Similarly, the two-body diagrams are similar to those in Fig. (2.6) but the bottom interaction, in the diagrams (b) to (g), is replaced by the cluster amplitude. After the attachment energy calculation, the excitation energy of a particular atomic state $|\Psi_{v'w'}\rangle$ is

$$\Delta E_{v'w'} = E_{v'w'} - E_{ns^{2} \, {}^1S_0},\tag{5.22}$$

where $E_{ns^2 \, {}^1S_0}$ is the ground state energy. We have used this equation and calculated the excitation energy for alkaline-earth metal atoms. These results are presented in the result section of the chapter.

5.3.2 Hyperfine structure constants

As mentioned in the previous chapter while discussing the one-valence systems, HFS constant is the expectation of the hyperfine interaction Hamiltonian with respect to the atomic state. Here we start with the Eq. (4.41), which is, after using the coupled-cluster wave function of two-valence atoms defined in Eq. (5.4)

$$\langle \Psi_i | H_{\rm hfs} | \Psi_i \rangle = \sum_{j,k} c_j^{i*} c_k^i \langle \Phi_i | e^{T^{\dagger}} \left[1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right]^{\dagger} H_{\rm hfs}$$

$$\times e^T \left[1 + S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right] | \Phi_k \rangle.$$

$$(5.23)$$

This is the CC expression to calculate the HFS constants of two-valence electron atoms. Using the dressed hyperfine operator $\tilde{H}_{\rm hfs}$, defined in Eq. (4.43), the expression simplifies to

$$\langle \Psi_i | H_{\rm hfs} | \Psi_i \rangle = \sum_{j,k} c_j^{i*} c_k^i \langle \Phi_j | \tilde{H}_{\rm hfs} + \tilde{H}_{\rm hfs} \left[S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right] + \\ \left[S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right]^{\dagger} \tilde{H}_{\rm hfs} + \left[S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right]^{\dagger} \\ \tilde{H}_{\rm hfs} \left[S_1^{(1)} + \frac{1}{2} S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)} \right] | \Phi_k \rangle.$$

$$(5.24)$$

As discussed in the one-valence case, comprehensive inclusion of terms of all order in T is beyond the scope of current theories and computational resources. Further more, the contribution from the terms higher than quadratic in T is $\approx 0.1\%$ of the total value. So we consider the dressed operator only up to quadratic in T. That is

$$\widetilde{H}_{\rm hfs} \approx H_{\rm hfs} + H_{\rm hfs}T + T^{\dagger}H_{\rm hfs} + T^{\dagger}H_{\rm hfs}T.$$
(5.25)

The diagrams contributing to the Eq. (5.25) are separated as effective one- and two-body operators. Diagrammatic representation of these effective operators are as shown in Fig. 4.12. It is important to note that the two-body effective operator, shown in Fig. 4.12(e), arises from the last term in Eq. (5.25). And, as it has two-orders of T, the hyperfine diagrams obtained after contraction with S may have negligible contributions.

5.3.2.1 The $\widetilde{H}_{\rm hfs}$ term

Only the last term i. e. $T^{\dagger}H_{\rm hfs}T$ in the truncated $\widetilde{H}_{\rm hfs}$ contribute to the HFS constants of the two-valence systems. There are four diagrams which has non-zero contribution from this term. These arise from $T_2^{\dagger}T_2$ with the bare hyperfine interaction $h_{\rm hfs}$ inserted to all the possible orbital lines. Contribution from these diagrams all together is expected to be very small as it does not involve S. Contribution from this term is separately given in the result section.

5.3.2.2 The
$$\widetilde{H}_{hfs}\left(S_1^{(1)} + \frac{1}{2}S_1^{(1)^2} + S_2^{(1)} + S_2^{(2)}\right) + h.c.$$
 term

There is one diagram each in the terms $\tilde{H}_{hfs}S_1^{(1)}$ and $S_1^{(1)}^{\dagger}\tilde{H}_{hfs}$. These arise from the contraction of the two-body effective operator, shown as Fig. 4.12(e), with the one-valence cluster operator. Similarly, $\tilde{H}_{hfs}S_1^{(1)^2}$ and its Hermitian conjugate contribute one diagram each. These are also from the two-body effective dressed hyperfine operator. Since the two-body effective operator involves two orders of T, the contribution form these diagrams is expected to be very small. The contributions from these are listed in the table presented in the result section of this chapter.

The $\widetilde{H}_{\rm hfs}S_2^{(1)}$ and $S_2^{(1)\dagger}\widetilde{H}_{\rm hfs}$ terms have one diagram each and these arise when $S_2^{(1)}$ is contracted with the one-body effective operators: $S_2^{(1)}$ with diagram in Fig. 4.12(d), and $S_2^{(1)\dagger}$ with diagram in Fig. 4.12(c). The diagram arising from $S_2^{(1)\dagger}\widetilde{H}_{\rm hfs}$ is shown in Fig. 5.6(a). Time reversed version of the same diagram correspond to $\widetilde{H}_{\rm hfs}S_2^{(1)}$, however, this is not shown in figure. The contributions from $\widetilde{H}_{\rm hfs}S^{(1)}$ and $S^{(1)\dagger}\widetilde{H}_{\rm hfs}$ are large as these are first order in S. Further more, $H_{\rm hfs}$ is one-body interaction and one-body effective interaction are large.



Figure 5.6: The actual hyperfine diagrams contributing to the terms, $S_2^{(1)^{\dagger}} \widetilde{H}_{hfs}$ (a), $S^{(2)^{\dagger}} \widetilde{H}_{hfs}$ (b), $S_2^{(1)^{\dagger}} \widetilde{H}_{hfs} S^{(2)}$ (c) to (e), and $S^{(2)^{\dagger}} \widetilde{H}_{hfs} S^{(2)}$ (f). The diagrams contributing to the corresponding Hermitian conjugate terms are the time reversed of these diagrams, and are not shown explicitly.

The $\tilde{H}_{\rm hfs}S_2^{(2)}$ and $S_2^{(2)}{}^{\dagger}\tilde{H}_{\rm hfs}$ terms also contribute one diagram each. These arise from the contraction of $S_2^{(2)}$ with the one-body effective operator of $\tilde{H}_{\rm hfs}$ shown in diagram Fig. 4.12(a). The diagram from $S^{(2)}{}^{\dagger}\tilde{H}_{\rm hfs}$ is shown in Fig. 5.6(b). Like in the previous case, the time reversed diagram arise from $\tilde{H}_{\rm hfs}S^{(2)}$ and is now shown in the figure. One can expect these terms to form the leading order as these are the lowest order terms with $S_2^{(2)}$. The two-valence cluster operator $S_2^{(2)}$ is in general larger in magnitude than the one-valence cluster operator.



Figure 5.7: Diagrams arising in contraction of $S_2^{(1)\dagger}$ with $S_2^{(1)}$.

5.3.2.3 The $S_1^{(1)\dagger} \widetilde{H}_{hfs} \left(S_1^{(1)} + \frac{1}{2} S_1^{(1)} + S_2^{(1)} + S_2^{(2)} \right)$ term

The first two terms contribute one diagram each through the two-body effective operator diagram Fig. 4.12(e). These are not shown here as they have negligible contribution. There are two diagrams which contribute to the term $S_1^{(1)\dagger} \tilde{H}_{hfs} S_2^{(1)}$. These arise from the contraction of the one-body effective operator diagram Fig. 4.12(d) with $S_2^{(1)}$ and $S_1^{(1)\dagger}$ connected at the two free lines. The last term also has contribution from two diagrams, arising in the contraction of $S_1^{(1)\dagger}$ and the effective operator diagram Fig. 4.12(a) with the two-valence cluster operator diagram. We have not shown these diagrams as the contribution, because of the $S_1^{(1)}$, is small.

5.3.2.4 The
$$S_1^{(1)2^{\dagger}} \widetilde{H}_{hfs} \left(S_1^{(1)} + \frac{1}{2} S_1^{(1)2} + S_2^{(1)} + S_2^{(2)} \right)$$
 term

The first term is the Hermitian conjugate of the term $S_1^{(1)}{}^{\dagger}\widetilde{H}_{\rm hfs}S_1^{(1)}{}^2$, described in the previous paragraph. And hence contributing diagram is the time reversed of those contributing to $S_1^{(1)}{}^{\dagger}\widetilde{H}_{\rm hfs}S_1^{(1)}{}^2$. There is only one diagram which contribute to the second term. We do not include this term in the actual calculation as there are four orders of $S_1^{(1)}$ involved. The third term contribute two diagrams, arising from the contraction of diagram Fig. 4.12(d) with $S_2^{(1)}$, and $S_1^{(1)}{}^{2\dagger}$ connected at the free lines in all possible ways. There is one diagram from the last term. This is expected to contribute large than the other diagrams which involve two orders of $S_1^{(1)}$.



Figure 5.8: Hyperfine diagrams obtained after inserting the Hyperfine interaction operator in diagram (b) of Fig. (5.7).

5.3.2.5 The
$$S_2^{(1)\dagger} \widetilde{H}_{hfs} \left(S_1^{(1)} + \frac{1}{2} S_1^{(1)} + S_2^{(1)} + S_2^{(2)} \right)$$
 term

The contributing diagrams in the first two terms are the time reversed of the those arising from the corresponding Hermitian conjugate terms discussed in the previous paragraphs. For this reason we do not discuss these terms.

There are sixteen diagram arising from $S_2^{(1)\dagger} \widetilde{H}_{hfs} S_2^{(1)}$. Topologically these are the effective one-body diagrams Fig. 4.12(a-b) sandwiched between $S_2^{(1)\dagger}$ and $S_2^{(1)}$. To examine the diagrams in more detail, all the diagrams (four in all) from $S_2^{(1)\dagger} S_2^{(1)}$ are shown in in Fig. 5.7. To each of the diagrams in Fig. 5.7 the effective one-body operator can be inserted in four ways. As an example, consider the diagram in Fig. 5.7(b), all the four diagrams after inserting the effective one-body operator are shown in Fig. 5.8. There are five diagrams from $S_2^{(1)\dagger} \widetilde{H}_{hfs} S_2^{(2)}$. These are arise from the contraction of $S_2^{(1)\dagger}$ with $S_2^{(2)}$ through one-body operators in Fig. 4.12(a) and (c). The diagrams from $S_2^{(1)\dagger} \widetilde{H}_{hfs} S_2^{(2)}$ are as shown in Fig. 5.6(c-e).

5.3.2.6 The
$$S_2^{(2)\dagger} \widetilde{H}_{hfs} \left(S_1^{(1)} + \frac{1}{2} S_1^{(1)} + S_2^{(1)} + S_2^{(2)} \right)$$
 term

The Hermitian conjugate terms corresponding to the first three terms were discussed in the previous paragraphs. So we do not consider these again. Only one diagram arises from the last term, $S_2^{(2)\dagger} \tilde{H}_{\rm hfs} S_2^{(2)}$. This diagram is shown in Fig. (5.6(f). Only Fig. 4.12(a) is the allowed effective one-body operator which contribute to this term. This term is expected to contribute the most as only one order of two-valence cluster operator is involved.

5.3.3 Electric dipole transition amplitudes

The E1 transition amplitude, as described in the context of the one-valence atoms in the previous chapter, is a matrix elements between two opposite parity states rather than the expectation in the HFS constants case. For two-valence atoms using the coupled-cluster wave function the E1 transition amplitude is derived, based on the Eq. (5.24), to the form

$$\langle \Psi_{f} \| D \| \Psi_{i} \rangle = \sum_{j,k} c_{j}^{f^{*}} c_{k}^{i} \langle \Phi_{j} | \tilde{D} + \tilde{D} \left[S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right] + \\ \left[S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right]^{\dagger} \tilde{D} + \left[S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right]^{\dagger} \\ \tilde{D} \left[S_{1}^{(1)} + \frac{1}{2} S_{1}^{(1)^{2}} + S_{2}^{(1)} + S_{2}^{(2)} \right] | \Phi_{k} \rangle.$$

$$(5.26)$$

As we see, Eq. (5.26) has the same structure as the Eq. (5.24) for HFS constants calculation. The only differences are the dipole operator replacing the hyperfine operator and it is the matrix elements not the expectation. The contributing diagrams are, therefore, same as those of the HFS constants. Hence, in actual calculation, we proceed like in HFS and calculate the effective diagrams, both one- and two-body. These are then contracted with the cluster operators to contribute to the transition matrix.

5.4 Summary of the results

In this section we present and analyze some of the atomic properties calculated from the relativistic two-valence CCT for two-valence atoms. Our results are based on the mathematical expressions that we provide in the previous sections of the chapter.

5.4.1 Excitation Energies

Results of the two-electron attachment and the excitation energies of Sr, Ba, and Yb atoms are listed in the Table. 5.1. For comparison the results from previous theoretical calculations and experimental data are also listed. The two-electron attachment energy is calculated using Eq. (5.21), however, to calculate the excitation energy we use Eq. (5.22). The reason for choosing the three atoms in our calculations is the significant difference in the sequences of $ns(n-1)d \ ^{3}D_{J}$, $ns(n-1)d \ ^{1}D_{2}$, $nsnp \ ^{3}P_{J}$ and $nsnp \ ^{1}P_{1}$ levels. As evident from Table. 5.1, in Sr the $5s4d \ ^{2S+1}D_{J}$ levels lies between $5s5p \ ^{3}P_{J}$ and $5s5p \ ^{1}P_{1}$. Whereas the $6s5d \ ^{2S+1}D_{J}$ levels are below the $6s6p \ ^{2S+1}P_{J}$ levels in Ba. The difference in the level structure can be attributed to the presence of an additional diffuse shell 4d. The sequence gets more complicated in Yb, $6s6p \ ^{3}P_{J}$ levels are below $6s5d \ ^{3}D_{J}$, however, the $6s6p \ ^{1}P_{1}$ lies between $6s5d \ ^{3}D_{2}$ and $6s5d \ ^{3}D_{3}$. It is to be noted that, the difference between Ba and Yb configurations is the presence of 4f in the Yb core. And, is the cause for the change in the level sequence.

In the case of atomic Sr, all the previous theoretical results listed in the table are with the atomic many-body methods different than ours. Porsev and collaborators [129] provides data for all the states we consider in our calculations. They have used the method which is a combination of the Configuration interaction and the many-body perturbation theory. The other available data is from the work of Savukov and Johnson [130] and Vaeck, Godfroid and Hansen [131]. The former is limited to the states 5s5p $^{3}P_{1}$ and 5s5p $^{1}P_{1}$, and they employed the same method as the work of Porsev and collaborators. However the single electron basis functions used in the two calculations are very different. And this may be the reason for the difference in the excitation energies of 5s5p ${}^{3}P_{1}$ and 5s5p ${}^{1}P_{1}$ states. The work of Vaeck and collaborators is limited to $5s4d {}^{1}D_{2}$ and $5s5p {}^{1}P_{1}$ and they have used the less accurate method, the multi-configuration Hartree-Fock (MCHF) theory. The excitation energies obtained from our calculations are reasonably close to the results of [129]. The difference, in all the states, is at the milihartree level. For the state $5s5p {}^{3}P_{2}$ our result is closest to the experimental value. Our results are consistently better than the MCHF results of the Ref. [131].

As its evident from the table, quite a few previous theoretical results are available for the atomic Ba. Among the results listed, the work of Eliav, Kaldor and Ishikawa [115] uses the method similar to ours. The single electron spinorbitals used in the calculations are generated in the same Vn - 2 potential. The other theoretical works of Dzuba and collaborators [132], and Safronova and collaborators [133] uses similar basis sets but different many-body methods. The former used CI-MBPT, whereas the later used the recently developed CI plus all order method [133]. The results from these two calculations are in better agreement with the experimental data than the results of the Eliav and

State	Our re	esult	Other work	Exp. $\operatorname{Ref}[63]$.
	<i>E</i>	ΕE	$\mathbf{E}\mathbf{E}$	\mathbf{EE}
		$^{87}\mathrm{Sr}$		
$5s^{2} {}^{1}S_{0}$	-0.61939	0.0	0.0	0.0
$5s5p \ {}^{3}P_{0}$	-0.55169	0.06771	0.06566^{a}	0.06524
$5s5p \ ^{3}P_{1}$	-0.55170	0.06768	$0.06651^{\rm a}, 0.06871^{\rm b}$	0.06609
$5s5p \ {}^{3}P_{2}$	-0.55203	0.06736	$0.06833^{\rm a}$	0.06788
$5s4d \ ^{3}D_{1}$	-0.53551	0.08388	$0.08230^{\rm a}$	0.08274
$5s4d \ ^{3}D_{2}$	-0.53478	0.08461	$0.08260^{\rm a}$	0.08301
$5s4d \ ^{3}D_{3}$	-0.53397	0.08542	$0.08312^{\rm a}$	0.08347
$5s4d \ ^{1}D_{2}$	-0.52594	0.09345	$0.09210^{\rm a}, 0.11477^{\rm c}$	0.09181
$5s4d \ ^{1}P_{1}$	-0.51283	0.10656	$0.09851^{\rm a}, 0.10015^{\rm b}, 0.10730^{\rm c}$	0.09887
2.4		137 Ba		
$6s^{2} {}^{1}S_{0}$	-0.56439	0.0	0.0	0.0
$6s5d \ ^{3}D_{1}$	-0.52303	0.04136	$0.04211^{\rm d}, 0.04106^{\rm e}, 0.04119^{\rm f}$	0.04116
$6s5d {}^{3}D_{2}$	-0.52170	0.04269	$0.04296^{\rm d}, 0.04193^{\rm e}, 0.04200^{\rm f}$	0.04199
$6s5d \ ^{3}D_{3}$	-0.51960	0.04479	$0.04473^{\rm d}, 0.04375^{\rm e}, 0.04366^{\rm f}$	0.04375
$6s5d \ ^{1}D_{2}$	-0.51030	0.05409	$0.05395^{\rm d}, 0.05197^{\rm e}, 0.05298^{\rm f}$	0.05192
$6s6p {}^{3}P_{0}$	-0.50667	0.05772	$0.05697^{\rm d}, 0.05575^{\rm e}, 0.05591^{\rm f}$	0.05589
$6s6p \ ^{3}P_{1}$	-0.50540	0.05899	$0.05869^{\rm d}, 0.05742^{\rm e}, 0.05758^{\rm f}$	0.05758
$6s6p \ {}^{3}P_{2}$	-0.50311	0.06128	$0.06284^{\rm d}, 0.06147^{\rm e}, 0.06159^{\rm f}$	0.06158
$6s6p \ ^{1}P_{1}$	-0.47291	0.09148	$0.08409^{\rm d}, 0.08256^{\rm e}, 0.08125^{\rm f}$	0.08229
		$^{173}\mathrm{Yb}$		
$6s^{2} {}^{1}S_{0}$	-0.68083	0.0	0.0	0.0
$6s6p \ {}^{3}P_{0}$	-0.59944	0.08140	$0.07909^{\rm g}, 0.07874^{\rm h}, 0.07877^{\rm i}$	0.07877
$6s6p {}^{3}P_{1}$	-0.59645	0.08439	$0.08242^{\rm g}, 0.08200^{\rm h}, 0.08200^{\rm i}$	0.08198
$6s6p \ {}^{3}P_{2}$	-0.58914	0.09170	$0.09038^{\rm g}, 0.08999^{\rm h}, 0.09002^{\rm i}$	0.08981
$6s5d \ ^{3}D_{1}$	-0.56110	0.11973	$0.11362^{\rm g}, 0.11425^{\rm h}, 0.11158^{\rm i}$	0.11158
$6s5d \ ^{3}D_{2}$	-0.55975	0.12109	$0.11473^{\text{g}}, 0.11136^{\text{h}}, 0.11274^{\text{i}}$	0.11278
$6s5d \ ^{3}D_{3}$	-0.55602	0.12481	$0.11699^{\rm g}, 0.11503^{\rm h}, 0.11517^{\rm i}$	0.11514
$6s6p \ ^{1}P_{1}$	-0.55301	0.12782	$0.12426^{\rm g}, 0.11253^{\rm h}, 0.11669^{\rm i}$	0.11422
$6s5d \ ^1D_2$	-0.54667	0.13416	$0.13025^{\rm g}, 0.12595^{\rm h}, 0.12672^{\rm i}$	0.12611

Table 5.1: Two-electron removal energy and the excitation energies calculated using relativistic coupled-cluster theory. All values are in atomic units.

^a Reference[129]. ^b Reference [130]. ^c Reference [131]. ^d Reference[115].

^e Reference[133]. ^f Reference [132]. ^g Reference[114]. ^h Reference[134].

ⁱ Reference[135].

ours. For some of the states, $6s5d \ ^3D_1$, $6s5d \ ^3D_2$, $6s6p \ ^3P_2$, our results are closer to the experiment than Eliav [115].

Like the atomic Ba, several attempts have been made to produce the correct energy level sequence and the accurate excitation energies of the states for atomic Yb. However, this presents a serious challenge. A similar calculation to ours [114] could not reproduced the experimental sequence. In particular, the $6s6p {}^{1}P_{1}$ is above the $6s5d {}^{3}D_{I}$ levels, whereas experimentally it lies between $6s5d \ ^{3}D_{2}$ and $6s5d \ ^{3}D_{3}$. The sequence, however, is correctly reproduced in another calculation with the CI-MBPT method [134], where the basis set used is combination of Dirac-Fock orbitals for the core and valence, and virtuals are generated through recurrent procedure. Our results show the similar energy level sequence as that of the Ref. [114]. However the excitation energies for all the states are systematically higher than the previous theoretical data. The excitation energies from the works [134] and [135] are better than [114]and ours for all the states. As its clear from the discussions, none of the results listed in the table follow the same atomic many-body methods and the single electron basis functions. This could be the reason of the observed inconsistency among the theoretical data. This atomic system, in our view, requires a systematic analysis and inclusion of the various correlation effects in the precision calculations.

5.4.2 Hyperfine structure constants

For the two-valence HFS calculations we have used the Eq. (5.24) describe in the previous section of the chapter. The results from our calculation are presented in the Table. 5.2. To compare and analyze, the results from previous theoretical works and experimental data are also given. As evident from the table, there are few theoretical and experimental work on the HFS constants of the neutral alkaline-Earth metal atoms and Yb. However, the importance of such investigations are likely grow in the near future as these, in particular Sr and Yb, are candidates of precision experiments and have been cooled to quantum degeneracy.

Unlike the case of one-valence atomic systems, the HFS contributions from different terms in the CC HFS equation, Eq. (5.24), are separated in to three groups. The second column, as in the one-valence atoms, comprise of the contributions from two terms: the zeroth-order and the terms with only closedshell cluster operators. The contribution from the later is far less, almost negligible, than the former for two-valence atoms. The next column presents the results from terms which involve the one-body effective dressed properties operator. And similarly, the last column lists the contributions from the term with the two-body effective dressed properties operator. As we have mentioned in the theoretical descriptions, the dominant contribution is from DF term for all the states in all the atoms considered. The second largest contribution is

Table 5.2: Magnetic dipole hyperfine structure constant for the atomic systems ⁸⁷Sr, ¹³⁷Ba and ¹⁷³Yb, using relativistic coupled-cluster. All values are in atomic units.

State		Coupled-clu	Others	Exp.		
	Ĩ	$\tilde{\mathbf{H}}$	$(\tilde{\mathbf{H}})$			
	$H_{ m hfs}$	$(H_{ m hfs})_{1b}$	$(H_{\rm hfs})_{2b}$	Total		
		$^{87}\mathrm{Sr}$				
$5s5p \ ^{3}P_{1}$	-179.103	-49.121	0.002	-228.222	_	$-260.765(1)^{j}$
$5s5p \ {}^{3}P_{2}$	-200.564	-47.045	0.002	-247.607	_	$-212.085(5)^{j}$
$5s4d \ ^{3}D_{1}$	145.433	6.348	0.001	151.586	_	_
$5s4d \ ^{3}D_{2}$	-56.748	7.095	0.001	-49.654	_	_
$5s4d \ ^{3}D_{3}$	-133.970	.194	0.002	-133.778	_	_
$5s4d \ ^1D_2$	17.503	9.643	0.001	27.145	_	_
$5s4d \ ^{1}P_{1}$	11.577	4.366	-0.002	15.941	_	_
		^{137}Ba				
$6s5d$ $^{3}D_{1}$	-588.088	-19.420	-0.004	-607.512	$-547^{\rm a}$	$-521^{\rm c}$
$6s5d \ ^{3}D_{2}$	396.863	9.067	-0.009	405.921	405^{a}	$416^{\rm c}$
$6s5d$ $^{3}D_{3}$	544.110	4.843	-0.008	548.945	443^{a}	$457^{\rm c}$
$6s5d \ ^{1}D_{2}$	-149.004	-54.967	-0.006	-203.977	$-102^{\rm a}$	$-82^{\rm d}$
$6s6p \ {}^{3}P_{1}$	735.756	221.943	-0.004	957.695	1160^{a}	1151^{e}
$6s6p \ {}^{3}P_{2}$	805.880	204.186	-0.010	1010.056	845^{a}	_
$6s6p \ ^{1}P_{1}$	-181.732	-38.353	0.009	-220.094	-107^{a}	-109^{f}
		173Vb				
$6s6n^3P_1$	$-709\ 145$	-197665	0.004	-906 806	-1094 ^b	$-1094\ 2(6)^{g}$
$6s6p^{-3}P_{0}$	-682.024	-181 832	0.001	-863.853	-745^{b}	$-738^{\rm h}$
$6s5d {}^{3}D_{1}$	550 714	64 941	0.000	615 657	596 ^b	$563(1)^{i}$
$6s5d {}^3D_0$	$-456\ 216$	-40.287	0.002	-496500	-351 ^b	$-362(2)^{i}$
$6s5d {}^{3}D_{2}$	-454 458	-22.482	0.002	-476938	-420^{b}	$-430(1)^{i}$
$6s6n {}^1P_1$	240 029	65 911	-0.002	305 938	191 ^b	60 ^h
$6s5d {}^{1}D_{2}$	$197\ 207$	71 840	0.002	269.049	131 ^b	$100(18)^{i}$
5550 D.2	101.201	11.010	0.002	200.010	101	100(10)

^a Reference[136]. ^b Reference[134]. ^c Reference[137]. ^d Reference[138]. ^e Reference[139]. ^f Reference[140]. ^g Reference[141]. ^h Reference[142].

ⁱ Reference 143. ^j Reference 144.

from the terms with the one-body effective operator. The contribution from the two-body HFS terms all together is very less in comparison to the previous two terms.

For the atomic Sr no theoretical data is available in the literature. The experimental results however are available for only two states $5s5p \ ^{3}P_{1}$ and $5s5p \ ^{3}P_{2}$. Our results for these two states differ by about 12% and 16.5% respectively, from the experimental values. Since there are not much data available its inappropriate to comment on the accuracy of these results. This atom needs to be investigated both theoretically and experimentally.

In the case of atomic Ba, the results of Kozlov and collaborators [136] are the only theoretical results we could obtain from the literature. As mentioned earlier, they employed a method which is a combination of the CI and the MBPT. Considering the experimental results, none of the states have data from the two different experiments. The results of Kozlov and collaborators [136] are, however, in better agreement than ours. In our results, the large discrepancy is observed in the singlet states, $6s6p \,{}^1P_1$ and $6s5d \,{}^1D_2$. The HFS constants for the state $6s5d \,{}^3D_2$ from our results are in agreement with the results of the Ref. [136].

Similar to the case of atomic Ba, the HFS constants of the atomic Yb there is a lack of theoretical and experimental studies. The only previous theoretical investigation in literature is the work of Porsev, Rakhlina and Kozlov [134]. Their results are in good agreement with the experimental data than ours. However, the atomic many-body method and the single-electron basis functions used in the two calculations are very different. The large discrepancy in the our results may be attributed to the nature of the orbitals we have used, the V^{N-2} orbitals. On account of the doubly ionized state of the core, the orbitals are highly contracted and interacts rather strongly with the nucleus. Such orbitals are suitable for properties calculations of singly ionized states but not an ideal choice for neutral atoms.

5.4.3 E1 transition amplitude

The electric dipole reduced matrix elements of the two-valence atoms Sr, Ba and Yb are presented in the Tables. 5.3, 5.4 and 5.5 respectively. In all the cases, like the HFS constants, contributions from different terms are grouped in to three categories. And the corresponding values are listed the tables. As evident from the tables, the individual contributions follow the same trend as the HFS constants. For all the atoms the dominant contribution is from the Dirac-Fock term. The next prominent contribution is from the effective one-body operator. And then the terms with only closed-shell cluster operators, $\tilde{D} - DF$ contributes. As mentioned in the HFS case, there is negligible contribution from the terms with the two-body effective operator.

Out of the transitions we have considered in our calculations, the previous

Table 5.3: E1 transition amplitudes for the atomic system $^{87}{\rm Sr},$ using relativistic coupled-cluster theory. All values are in atomic units.

Transition	Coupled-cluster terms					
	DF	$\tilde{D} ext{-}\mathrm{DF}$	$(\tilde{D})_{1b}$	$(\tilde{D})_{2b}$	Total	
${}^{3}P_{1} \rightarrow {}^{1}S_{0}$	-0.3759	-0.0001	0.8257	0.00001	0.4497	$0.16^{\rm a},$
						$0.162^{\rm b}$
${}^{1}P_{1} \rightarrow {}^{1}S_{0}$	-4.2442	0.0000	0.5283	-0.00002	-3.7159	$5.28^{\rm a}$,
						$5.238^{\rm b},$
						1.9539^{c}
${}^{3}P_{0} \rightarrow {}^{3}D_{1}$	2.6323	-0.0002	-0.3131	0.00000	2.3190	
${}^{3}P_{1} \rightarrow {}^{3}D_{1}$	2.2652	0.0013	0.1116	0.00000	2.3781	
${}^{3}P_{2} \rightarrow {}^{3}D_{1}$	0.5849	0.0009	0.3772	-0.00001	0.9630	
${}^1P_1 \rightarrow {}^3D_1$	0.2255	-0.0005	-0.2496	-0.00001	-0.0247	
${}^{3}P_{1} \rightarrow {}^{3}D_{2}$	3.9538	0.0012	-0.5437	-0.00001	3.4114	
${}^{3}P_{2} \rightarrow {}^{3}D_{2}$	2.2646	0.0006	0.0700	0.00001	2.3352	
$^{1}P_{1} \rightarrow ~^{3}D_{2}$	0.7531	-0.0004	-0.1054	0.00001	0.6473	
${}^{3}P_{2} \rightarrow {}^{3}D_{3}$	-5.3938	-0.0001	0.3111	0.00001	-5.0828	
${}^{3}P_{1} \rightarrow {}^{1}D_{2}$	-0.8822	0.0012	0.0387	0.00000	-0.8423	$0.19^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{1}D_{2}$	-0.2854	0.0002	-0.3597	-0.00001	-0.6448	$0.10^{\rm a}$
${}^1P_1 \rightarrow {}^1D_2$	-4.5484	-0.0008	0.3860	-0.00001	-4.1632	$1.92^{\rm a}$

^a Reference[129]. ^b Reference[130]. ^c Reference[131].

Table 5.4: E1 transition amplitudes for the atomic system 137 Ba, using relativistic coupled-cluster theory. All values are in atomic units.

Transition		Other work				
	DF	$\tilde{D} ext{-}\mathrm{DF}$	$(\tilde{D})_{1b}$	$(\tilde{D})_{2b}$	Total	
${}^{3}P_{1} \rightarrow {}^{1}S_{0}$	0.3888	-0.0003	-0.8090	0.00000	0.4205	$0.4537^{\rm a}$
${}^{1}P_{1} \rightarrow {}^{1}S_{0}$	-4.6768	-0.0002	0.6730	0.00000	4.0040	$5.236^{\rm a}$
${}^{3}P_{0} \rightarrow {}^{3}D_{1}$	2.6203	0.0004	-0.2585	0.00000	2.3622	$2.3121^{\rm a}$
${}^{3}P_{1} \rightarrow {}^{3}D_{1}$	2.2405	-0.0023	-0.0195	0.00000	2.2187	$2.0108^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{3}D_{1}$	-0.5715	0.0019	-0.4782	0.00000	1.0478	$0.5275^{\rm a}$
${}^{1}P_{1} \rightarrow {}^{3}D_{1}$	-0.3364	-0.0002	0.3546	0.00000	0.0180	$0.1047^{\rm a}$
${}^{3}P_{1} \rightarrow {}^{3}D_{2}$	3.8886	-0.0022	-0.1585	0.00001	3.7279	$3.4425^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{3}D_{2}$	-2.2265	0.0013	0.1007	-0.00001	2.1245	$2.024^{\rm a}$
${}^1P_1 \rightarrow {}^3D_2$	-0.3874	-0.0005	0.0833	-0.00000	0.3046	$0.4827^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{3}D_{3}$	5.3410	-0.0004	-0.3409	-0.00001	4.9997	$4.777^{\rm a}$
${}^{3}P_{1} \rightarrow {}^{1}D_{2}$	-1.1039	-0.0018	0.1178	0.00000	0.9879	$0.1610^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{1}D_{2}$	0.4458	0.0005	0.5219	0.00001	0.9682	$0.1573^{\rm a}$
$^{1}P_{1} \rightarrow ~^{1}D_{2}$	4.4933	-0.0011	-0.0773	0.00000	4.4149	$1.047^{\rm a}$

^a Reference[132].

Transition		Others				
	DF	$\tilde{D} ext{-}\mathrm{DF}$	$(\tilde{D})_{1b}$	$(\tilde{D})_{2b}$	Total	
${}^{3}P_{1} \rightarrow {}^{1}S_{0}$	0.1445	-0.0003	-0.5320	0.00000	-0.3878	$0.54(8)^{\mathrm{a}},$
						$0.44^{\text{b}},$
						0.587°
$^{1}P_{1} \rightarrow ~^{1}S_{0}$	-3.8641	-0.0001	0.5999	-0.00001	-3.2643	$4.40(80)^{\mathrm{a}},$
						4.44 ^b ,
						4.89ª,
2 2 2 2		0.0001			0 4000	4.825 ^c
${}^{3}P_{0} \rightarrow {}^{3}D_{1}$	2.7296	0.0001	-0.3209	0.00000	2.4088	$2.61(10)^{\mathrm{a}},$
20 20		0 0 0 0 7	0 1 0 1 1			2.911 ^e
${}^{3}P_{1} \rightarrow {}^{3}D_{1}$	2.3473	-0.0005	0.1811	0.00003	2.5279	$2.26(10)^{a}$
$^{3}P_{2} \rightarrow ~^{3}D_{1}$	-0.5997	0.0000	-0.2343	0.000002	-0.8340	$0.60(12)^{\rm a}$
$^{1}P_{1} \rightarrow ~^{3}D_{1}$	-0.4503	-0.0002	0.1702	0.00000	-0.2803	$0.27(10)^{\mathrm{a}},$
						0.24^{b}
${}^{3}P_{1} \rightarrow {}^{3}D_{2}$	3.9875	-0.0005	-0.6480	0.00002	3.3390	$4.03(16)^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{3}D_{2}$	-2.2940	-0.0002	-0.1010	-0.00003	-2.3952	$2.39(1)^{a}$
$^{1}P_{1} \rightarrow ~^{3}D_{2}$	0.0716	-0.0003	0.0660	0.00000	0.1373	$0.32(6)^{\mathrm{a}},$
						0.60^{b}
${}^{3}P_{2} \rightarrow {}^{3}D_{3}$	5.6130	0.0000	-0.3215	-0.00001	5.2915	$6.12(30)^{a}$
${}^{3}P_{1} \rightarrow {}^{1}D_{2}$	-1.1920	-0.0006	0.0995	0.00000	-1.0931	$0.54(10)^{\rm a}$
${}^{3}P_{2} \rightarrow {}^{1}D_{2}$	0.5946	0.0002	0.3601	0.00000	0.9549	$0.38(8)^{a}$
${}^{1}P_{1} \rightarrow {}^{1}D_{2}$	4.7006	-0.0002	-0.5209	0.00000	4.1795	$3.60(70)^{\rm a}$

Table 5.5: E1 transition amplitudes for the atomic system 173 Yb, using relativistic coupled-cluster theory. All values are in atomic units.

^a Reference[145]. ^b Reference[146]. ^c Reference[135]. ^d Reference[147].

theoretical results are limited to $\langle 4s4p \ {}^{3}P_{1} \| D \| 4s^{2} \ {}^{1}S_{0} \rangle$, $\langle 4s4p \ {}^{1}P_{1} \| D \| 4s^{2} \ {}^{1}S_{0} \rangle$, $\langle 4s4p \ {}^{3}P_{1} \| D \| 4s4d \ {}^{1}D_{2} \rangle$, $\langle 4s4p \ {}^{3}P_{2} \| D \| 4s4d \ {}^{1}D_{2} \rangle$, and $\langle 4s4p \ {}^{1}P_{1} \| D \| 4s4d \ {}^{1}D_{2} \rangle$, for the atomic Sr. These are calculated using atomic many body methods significantly different than ours. Our results show large deviation from the previous theoretical values. In the case of Ba, the previous theoretical calculations were done by Dzuba and Ginges [132]. They have used the combined CI+MBPT. The single electron spin orbitals are g enerated in the V_{N-2} potential, which is similar to the ours. The best agreement is for the transitions $\langle 6s6p \ {}^{3}D_{1} \| D \| 6s^{2} \ {}^{1}S_{0} \rangle$ and $\langle 6s6p \ {}^{3}D_{J} \| D \| 6s5d \ {}^{3}D_{J} \rangle$. There are large deviations for the matrix elements involving the $6s6p \ {}^{1}P_{1}$ and $6s5d \ {}^{1}D_{2}$ states.

In comparison to Sr and Ba there are quite a few theoretical data of the E1 reduced matrix elements of atomic Yb. For some of the transitions our results are in good agreement with the previous works. Our results for $\langle 6s6p \ ^{3}P_{0} \| D \| 6s5d \ ^{3}D_{1} \rangle$, $\langle 6s6p \ ^{3}P_{1} \| D \| 6s5d \ ^{3}D_{1} \rangle$, $\langle 6s6p \ ^{1}P_{1} \| D \| 6s5d \ ^{3}D_{1} \rangle$, and $\langle 6s6p \ ^{3}P_{2} \| D \| 6s5d \ ^{3}D_{2} \rangle$, compare well with that of Porsev and collaborators [145]. The large deviations are however observed in the transitions $\langle 6s6p \ ^{1}P_{1} \| D \| 6s^{2} \ ^{1}S_{0} \rangle$, $\langle 6s6p \ ^{3}P_{1} \| D \| 6s5d \ ^{3}D_{2} \rangle$, $\langle 6s6p \ ^{3}P_{2} \| D \| 6s5d \ ^{3}D_{3} \rangle$, and $\langle 6s6p \ ^{3}P_{1} \| D \| 6s^{5}d \ ^{1}D_{2} \rangle$. These discrepancies are partly attributed to the different atomic many-body methods used in the two calculations. And partly to the nature of the potential used to generate the orbitals.

Chapter 6

Coupled-cluster theory with PNC perturbation

In the previous chapters we studied relativistic CCT of closed-shell, onevalence and two-valence atomic systems for the Dirac-Coulomb Hamiltonian. However, there are atomic properties of interest which are associated with external perturbations, for example an atom in electromagnetic fields. In the context of the atomic many-body theories, these additional interactions are treated as perturbations to the atomic Hamiltonian. These modify the wave function and energy of the atom. The precise calculations of the relevant atomic properties require a systematic inclusion of the correlation effects arising from the perturbation. The perturbed coupled cluster method is the appropriate one. In this chapter we discuss and derived the perturbed CC equations for closed-shell, one- and two-valence atoms. We also describe the scheme to calculate the E1PNC transition amplitudes using perturbed CC wave function.

This chapter is organize as follows. The first Section deal with the closedshell atomic systems with the perturbation. In particular, we treat the PNC electron-nucleus as perturbation and the closed-shell perturbed CC equations are derived. Sec. II describes the implementation of the perturbed CC theory of one-valence atoms. This is applied to calculate the E1PNC transition amplitudes in the same section. The perturbed CC method and application to calculate E1PNC of two-valence atomic systems is discussed in Sec. III. And the last Section is about the analysis of the results.

6.1 Closed-shell systems

There are several closed-shell atoms which are of experimental interests and have important implications to new physics. Perhaps among all the experiments, the electric dipole moment (EDM) of the atoms originating from the hadron sector [112, 148, 149] is the most important one. To extract new physics



Figure 6.1: Representation of the single and double perturbed cluster operators contributing at the level of closed-shell perturbed CC.

from the experimental and theoretical results, it essential that the two should be of comparable accuracy. And for the theoretical calculations with CCT, the perturbed CC theory plays an important role. In this section we derive the perturbed CC equations and use the wave function to calculate the dipole polarizibility of the inert-gas atoms.

6.1.1 Perturbed CC equations

In presence of the PNC interaction Hamiltonian H_{PNC} , the Schroedinger equation of closed-shell atoms is

$$\left(H^{\rm DC} + \lambda H_{\rm PNC}\right) |\widetilde{\Psi}_0\rangle = \widetilde{E} |\widetilde{\Psi}_0\rangle. \tag{6.1}$$

Here $|\tilde{\Psi}_0\rangle$ is the perturbed wave function, $\tilde{E}_{,} = E + \lambda E^1$, is the corresponding eigenvalue and λ is the perturbation parameter. The perturbed wave function is the sum of the unperturbed wave function and a correction $|\overline{\Psi}_0^1\rangle$ arising from H_{PNC} . That is

$$|\widetilde{\Psi}_0\rangle = |\Psi_0\rangle + \lambda |\overline{\Psi}_0^1\rangle. \tag{6.2}$$

Following the description of closed-shell unperturbed coupled-cluster wave function, the perturbed wave function in the coupled-cluster is

$$|\widetilde{\Psi}_0\rangle = e^{T^{(0)} + \lambda T^{(1)}} |\Phi_0\rangle.$$
(6.3)

The cluster operator $T^{(0)}$ is the unperturbed operator. The cluster operator $T^{(1)}$, however, incorporates the effect of $H_{\rm PNC}$ and is referred to as the perturbed CC operator. It acts on the reference state $|\Phi_0\rangle$ to generate the correction. Considering the perturbation expansion to first order in λ , we can write Eq. (6.3) as

$$|\tilde{\Psi}_0\rangle = e^{T^{(0)}} (1 + \lambda T^{(1)}) |\Phi_0\rangle.$$
 (6.4)

Using Eq. (6.4) in Eq. (6.1)

$$\left(H^{\rm DC} + \lambda H_{\rm PNC}\right) e^{T^{(0)}} \left[1 + \lambda T^{(1)}\right] \left|\Phi_0\right\rangle = E e^{T^{(0)}} \left[1 + \lambda T^{(1)}\right] \left|\Phi_0\right\rangle, \qquad (6.5)$$



Figure 6.2: Diagrams which contribute to the perturbed coupled-cluster equation for singles at the linear level.

where we have used the relation $E^1 = \langle \Psi_0 | H_1 | \Psi_0 \rangle = 0$, as H_{PNC} is an odd parity operator it does not connect states of same parity. Using the normalordered form of the Hamiltonian, $H_{\text{N}} = H - \langle \Phi_0 | H | \Phi_0 \rangle$, above equation can be be simplified to

$$(H_{\rm N} + \lambda H_{\rm PNC}) e^{T^{(0)}} \left[1 + \lambda T^{(1)} \right] |\Phi_0\rangle = \Delta E e^{T^{(0)}} \left[1 + \lambda T^{(1)} \right] |\Phi_0\rangle, \qquad (6.6)$$

where ΔE is the correlation energy of the atom. The terms which are first-order in λ is

$$\left[H_{\rm N}T^{(1)} + H_{\rm PNC}\right]e^{T^{(0)}}|\Phi_0\rangle = \Delta E T^{(1)}e^{T^{(0)}}|\Phi_0\rangle.$$
(6.7)

Operating with $e^{-T^{(0)}}$ and projecting on singly and doubly excited states $\langle \Phi_a^p \rangle$ and $\langle \Phi_{ab}^{pq} \rangle$, we get the working equations of the singles and doubles perturbed cluster amplitudes

$$\langle \Phi_a^p | \{ \overline{\bar{H}_N T}^{(1)} \} | \Phi_0 \rangle = - \langle \Phi_a^p | \overline{H}_{PNC} | \Phi_0 \rangle, \qquad (6.8)$$

$$\langle \Phi_{ab}^{pq} | \{ \bar{H}_{\rm N} T^{(1)} \} | \Phi_0 \rangle = - \langle \Phi_{ab}^{pq} | \bar{H}_{\rm PNC} | \Phi_0 \rangle.$$

$$(6.9)$$

The dressed Hamiltonian $\bar{H}_{\rm N}$ is same as in Eq. (4.10).

6.1.2 Linearized perturbed CC equations

The dressed Hamiltonian's, $\bar{H}_{\rm N}$ and $\bar{H}_{\rm PNC}$, in the linear approximation are

$$\bar{H}_{\rm N} = H_{\rm N} + \{ H_{\rm N} T^{(0)} \},$$
 (6.10)

$$\bar{H}_{PNC} = H_{PNC} + \{\dot{H}_{PNC}\dot{T}^{(1)}\}.$$
 (6.11)



Figure 6.3: Diagrams which contribute to the perturbed coupled-cluster equation for doubles at the linear level.

Using the above approximations in Eqs. (6.8) and (6.9), we get the perturbed coupled-cluster equations of singles and doubles in the CCSD approximation as

$$\langle \Phi_{a}^{p} | \{ \overline{H_{N}} T_{1}^{(1)} \} + \{ \overline{H_{N}} T_{2}^{(1)} \} | \Phi_{0} \rangle = -\langle \Phi_{a}^{p} | H_{PNC} + \{ \overline{H_{PNC}} T_{1}^{(0)} \}$$

$$+ \{ \overline{H_{PNC}} T_{2}^{(0)} \} | \Phi_{0} \rangle, \qquad (6.12)$$

$$\langle \Phi_{ab}^{pq} | \{ \overline{H_{N}} T_{1}^{(1)} \} + \{ \overline{H_{N}} T_{2}^{(1)} \} | \Phi_{0} \rangle = -\langle \Phi_{ab}^{pq} | H_{PNC} + \{ \overline{H_{PNC}} T_{1}^{(0)} \}$$

$$+ \{ \overline{H_{PNC}} T_{2}^{(0)} \} | \Phi_{0} \rangle. \qquad (6.13)$$

Diagrams corresponding to the left- and right-hand sides of the singles equation are shown in the Figs. 6.2 and 6.4 respectively. And the those corresponding to the doubles equation are shown in Figs. 6.3 and 6.5.



Figure 6.4: Coupled-cluster diagrams which contribute to the right-hand side of the Eq. (6.8). The line terminated with the square represent the H_{PNC} operator.

opposite parity states rather than the e



Figure 6.5: Coupled-cluster diagrams which contribute to the right-hand side of the Eq. (6.9). The line terminated with square is to represent the PNC interaction.

6.1.3 Dipole polarizibility from CCT

We calculate the dipole polarizibility to test the quality of the unperturbed and perturbed wave functions. When an atom is subjected to an external electric field \mathcal{E} , it induces a dipole to the atom. The induced dipole moment is

$$\boldsymbol{D}_{\text{induced}} = \alpha \mathcal{E}, \tag{6.14}$$

where α is the dipole polarizibility of the atom. In terms of the perturbed CC wave function it is the expectation of the dipole operator in the perturbed atomic states. That is

$$\alpha = \langle \widetilde{\Psi}_0 | \boldsymbol{D} | \widetilde{\Psi}_0 \rangle. \tag{6.15}$$

Using the form of the perturbed CC wave function from Eq. (6.3), we get

$$\alpha = \langle \Phi_0 | e^{T^{(0)}^{\dagger}} (1 + \lambda T^{(1)})^{\dagger} \mathbf{D} e^{T^{(0)}} (1 + \lambda T^{(1)}) | \Phi_0 \rangle,
= \langle \Phi_0 | \overline{D} + \overline{D} T^{(1)} + T^{(1)}^{\dagger} \overline{D} + T^{(1)}^{\dagger} \overline{D} T^{(1)} | \Phi_0 \rangle.$$
(6.16)

This the expression of the dipole polarizibility using CCT. In the above equation, the operator $\overline{D} = e^{T^{(0)}^{\dagger}} D e^{T^{(0)}}$ is the unitary transformed electric dipole operator and is usually refereed to as the dressed dipole operator. It is evident that the dipole polarizibility, in terms of perturbed cluster operator, distinctly different from the sum over states approach. In the sum over states scheme, contributions from a selected set of intermediates states are summed over. This is, however, not recommended for high precision calculations. In Eq. (6.16), contributions from all intermediate states within the chosen configuration space are included. For precision calculations, this is a very important advantage.

The diagrams contributing to the Eq. (6.16) are obtained by using the Wick's theorem. Contraction should be made in such a way that there should be no free lines at any of the vertices. In our studies, we also examine the contribution from the approximate triples. In the Fig. 6.6 we have shown an example diagram for each of the approximate triples and the dipole polarizibility.



Figure 6.6: Diagrams of approximate triples calculated perturbatively:(a) (a) Representation of approximate perturbed triples. (b) Contribution of approximate perturbed triples to the dipole polarizibility.

6.2 One-valence systems

For one-valence atoms, the E1PNC transition amplitudes [26, 25, 24, 31, 151] and the atomic EDM arising from the electron EDM [71, 154] are some of the important atomic properties of current interests. These require precise atomic theory calculations and the one-valence perturbed CC method is an ideal choice for these calculations. In this section we derive the perturbed CC equations and employ it to compute E1PNC of selected one-valence ions.

6.2.1 Perturbed CC equation from exponential ansatz

Following the perturbed Schroedinger equation of the closed-shell atoms, Eq. (6.1), the equation for one-valence systems is

$$(H + \lambda H_{\rm PNC}) |\tilde{\Psi}_v\rangle = (E_v + \lambda E_v^1) |\tilde{\Psi}_v\rangle, \qquad (6.17)$$

where the first-order energy correction $E_v^1 = \langle \Psi_v | H_{\text{PNC}} | \Psi_v \rangle = 0$. In the CCT the mixed parity state is describe using the cluster operators

$$|\widetilde{\Psi}_v\rangle = e^T \left(1 + \lambda T^{(1)}\right) \left(1 + S + \lambda S^{(1)}\right) |\Phi_v\rangle, \qquad (6.18)$$

where $|\Phi_v\rangle$ is the one-valence reference state. The newly introduced cluster operator $S^{(1)}$ is referred to as the one-valence perturbed CC operator. Using Eq. (6.18 in Eq. (6.17)

$$(H + \lambda H_{\text{PNC}}) e^{T} \left(1 + \lambda T^{(1)} \right) \left(1 + S + \lambda S^{(1)} \right) |\Phi_{v}\rangle$$
$$= E_{v} e^{T} \left(1 + \lambda T^{(1)} \right) \left(1 + S + \lambda S^{(1)} \right) |\Phi_{v}\rangle.$$
(6.19)

Operating above equation with e^{-T} and retaining the terms which are first-order in λ , we get

$$\left[e^{-T} H e^{T} S^{(1)} + e^{-T} H e^{T} T^{(1)} (1+S) + e^{-T} H_{\text{PNC}} e^{T} (1+S) \right] |\Phi_{v}\rangle$$

= $\left[E_{v} S^{(1)} + E_{v} T^{(1)} (1+S) \right] |\Phi_{v}\rangle.$ (6.20)

Using normal-ordered form of the Hamiltonian, $H_{\rm N} = H - \langle \Phi_v | H | \Phi_v \rangle$, we can further write

$$\begin{bmatrix} \bar{H}_{\rm N} S^{(1)} + \bar{H}_{\rm N} T^{(1)} (1+S) + \bar{H}_{\rm PNC} (1+S) \end{bmatrix} |\Phi_v\rangle = \begin{bmatrix} \Delta E_v S^{(1)} + \Delta E_v T^{(1)} (1+S) \end{bmatrix} |\Phi_v\rangle,$$
(6.21)

where $\Delta E_v = E_v - \langle \Phi_v | H | \Phi_v \rangle$, is the correlation energy of the one-valence atom. Projecting Eq. (6.21) with the excited determinants $\langle \Phi_v^p |$ and $\langle \Phi_{va}^{pq} |$, we get the perturbed CC equations of the singles and doubles respectively. These are

$$\langle \Phi_v^p | \bar{H}_N S^{(1)} + \bar{H}_N T^{(1)} (1+S) + \bar{H}_{PNC} (1+S) | \Phi_v \rangle = \Delta E_v \langle \Phi_v^p | S_1^{(1)} | \Phi_v \rangle, \quad (6.22)$$

$$\langle \Phi_{vw}^{pq} | \bar{H}_{N} S^{(1)} + \bar{H}_{N} T^{(1)} (1+S) + \bar{H}_{PNC} (1+S) | \Phi_{vw} \rangle = \Delta E_{v} \langle \Phi_{vw}^{pq} | S_{2}^{(1)} | \Phi_{vw} \rangle.$$
 (6.23)

In deriving above equations we have used the relations,

$$\langle \Phi_v^p | T^{(1)} | \Phi_v \rangle = 0 \quad \text{and} \quad \langle \Phi_v^p | T^{(1)} S | \Phi_v \rangle = 0,$$
 (6.24)

as $T^{(1)}$, being the cluster operator of closed-shell sector, does not contribute to the CC equation of $S_1^{(1)}$. The same is also true for the doubles. Using Wick's theorem the CC Eqs. (6.22) and (6.23), can further be simplified to the form

$$\langle \Phi_{v}^{p} | \{ \bar{H}_{N} S^{(1)} \} + \{ \bar{H}_{N} T^{(1)} \} + \{ \bar{H}_{N} T^{(1)} S \} + \{ \bar{H}_{PNC} (1+S) \} | \Phi_{v} \rangle$$

$$= E_{v}^{\text{att}} \langle \Phi_{v}^{p} | S_{1}^{(1)} | \Phi_{v} \rangle, \quad (6.25)$$

$$\langle \Phi_{vw}^{pq} | \{ \bar{H}_{N} S^{(1)} \} + \{ \bar{H}_{N} T^{(1)} \} + \{ \bar{H}_{N} T^{(1)} S \} + \{ \bar{H}_{PNC} (1+S) \} | \Phi_{v} \rangle$$

$$= E_{v}^{\text{att}} \langle \Phi_{v}^{p} | S_{2}^{(1)} | \Phi_{vw} \rangle.$$
(6.26)

where E_v^{att} is the attachment energy of the valence electron and is described in Eq. (4.35). In Eqs. (6.25) and (6.26), the disconnected terms $\{H_N T^{(1)}\}$ and $\{H_N T^{(1)}S\}$ do not contribute to the CC equations of single and double cluster operators.

6.2.2 Perturbed CC equations from Bloch equation

In the presence of PNC perturbation Hamiltonian the Bloch equation, Eq. (5.11), assumes the form

$$\left[\Omega + \lambda \Omega_{\rm PNC}, H_0\right] P = \left((V + \lambda H_{\rm PNC})(\Omega + \lambda \Omega_{\rm PNC}) - (6.27) \right)$$

$$(\Omega + \lambda \Omega_{\rm PNC})(W + \lambda W_{\rm PNC})P.$$
 (6.28)



Figure 6.7: Representation of the single and double perturbed cluster operators contributing at the level of one-valence perturbed CC.

Following Eq. (5.10), in the above equation

$$W_{\rm PNC} = P(V\Omega_{PNC} + H_{\rm PNC}\Omega)P = 0, \qquad (6.29)$$

as $W_{\rm PNC}$ acts within the same model space and the operators Ω_{PNC} and $H_{\rm PNC}$ connects states of opposite parity. To obtain the Bloch equation appropriate for the perturbed CCT retain terms linear in λ from the above equation. We then get

$$[\Omega_{\rm PNC}, H_0] P = \left(V \Omega_{\rm PNC} + H_{\rm PNC} \Omega - \Omega_{\rm PNC} W \right) P.$$
(6.30)

Using the CC wave operators

$$\Omega = e^{T}(1+S) \quad \text{and} \quad \Omega_{\text{PNC}} = e^{T}(T^{(1)} + S^{(1)} + T^{(1)}S), \tag{6.31}$$

the Eq. (6.30) assumes the form

$$\left[e^{T}(T^{(1)} + S^{(1)} + T^{(1)}S), H_{0}\right] |\Phi_{v}\rangle = \left(Ve^{T}(T^{(1)} + S^{(1)} + T^{(1)}S) + H_{\text{PNC}}e^{T}(1+S) - e^{T}(T^{(1)} + S^{(1)} + T^{(1)}S)W\right) |\Phi_{v}\rangle.$$
(6.32)

Following the derivation, Eq. (5.13), of the previous chapter, in the right-hand side of Eq. (6.32)

$$Ve^T = (Ve^T)_{\text{conn}} e^T = \overline{V}e^T$$
, and (6.33)

$$H_{\rm PNC}e^T = \bar{H}_{\rm PNC}e^T. (6.34)$$

Using Eqs. (6.33) and (6.34) and removing e^T from both side of the equations, we get

$$\left[T^{(1)} + S^{(1)} + T^{(1)}S, H_0\right]_{\text{conn}} |\Phi_v\rangle = \left[\bar{V}(T^{(1)} + S^{(1)} + T^{(1)}S) + \bar{H}_{\text{PNC}}(1+S) - (T^{(1)} + S^{(1)} + T^{(1)}S)W\right]_{\text{conn}} |\Phi_v\rangle.$$
(6.35)

We have retained only connected terms in this equation based on the argument given in the chapter. IV. The CC equation of singles is obtained by projecting this equation with the excited determinant $\langle \Phi_v^p |$.

$$\langle \Phi_v^p | \left[T^{(1)} + S^{(1)} + T^{(1)}S, H_0 \right]_{\text{conn}} | \Phi_v \rangle = \langle \Phi_v^p | \left[\bar{V}(T^{(1)} + S^{(1)} + T^{(1)}S) + \bar{H}_{\text{PNC}}(1+S) - (T^{(1)} + S^{(1)} + T^{(1)}S)W \right]_{\text{conn}} | \Phi_v \rangle. (6.36)$$

To simplify it further, various terms in Eq. (6.36) are derived in the following way. The left-hand side of this equation is

$$\langle \Phi_v^p | \left[T^{(1)} + S^{(1)} + T^{(1)}S, H_0 \right]_{\text{conn}} | \Phi_v \rangle = \langle \Phi_v^p | \left[S^{(1)}, H_0 \right] | \Phi_v \rangle, \quad (6.37)$$

as the closed-shell cluster operator $T^{(1)}$ can not contract with H_0 and contribute to the $S_1^{(1)}$ equation. Similarly, for the other terms

$$\langle \Phi_v^p | \bar{V} T^{(1)} | \Phi_v \rangle_{\text{conn}} = \langle \Phi_v^p | \{ V T^{(1)} \} | \Phi_v \rangle, \qquad (6.38)$$

$$\langle \Phi_v^p | \bar{V} T^{(1)} S | \Phi_v \rangle_{\text{conn}} = \langle \Phi_v^p | \{ \stackrel{\perp}{V} \stackrel{\perp}{T}^{(1)} \stackrel{\cdot}{S} \} | \Phi_v \rangle,$$

$$(6.39)$$

$$\langle \Phi_v^p | T^{(1)} W | \Phi_v \rangle = 0$$

$$\langle \Phi_v^p | T^{(1)} W | \Phi_v \rangle_{\text{conn}} = 0, \tag{6.40}$$

$$\langle \Phi_v^p | S^{(1)} W | \Phi_v \rangle_{\text{conn}} = \langle \Phi_v^p | \{ S^{(1)} W \} | \Phi_v \rangle_{\text{conn}}.$$
(6.41)

Using Eqs. (6.37) - (6.41), Eq. (6.36) is simplified to the form

$$\langle \Phi_v^p | \{ \overline{H}_N T^{(1)} \} + \{ \overline{H}_N S^{(1)} \} + \{ \overline{H}_N T^{(1)} S \} + \{ \overline{H}_{PNC} (1+S) \} | \Phi_v \rangle = (6.42)$$

$$H_{\text{eff}}\langle \Phi_v^p | S_1^{(1)} | \Phi_v \rangle. \quad (6.43)$$

Where we have used the relations

$$H_0 = \bar{H}_0 , \ \bar{H}_0 + \bar{V} = \bar{H}_N , \ \bar{V}T^{(1)}(1+S) = \bar{H}_N T^{(1)}(1+S),$$
(6.44)

as no closed-shell cluster contributes to CC $S^{(1)}$ equation after contraction with the open-shell cluster operator or with the H_0 . The same is true when T or $T^{(1)}$ contract with the renormalization term W. Following the same procedure, for doubles as

$$\langle \Phi_{vw}^{pq} | \{ \overline{H}_{N} T^{(1)} \} + \{ \overline{H}_{N} S^{(1)} \} + \{ \overline{H}_{N} T^{(1)} S \} + \{ \overline{H}_{PNC} (1+S) \} | \Phi_{vw} \rangle = (6.45)$$
$$H_{eff} \langle \Phi_{vw}^{pq} | S_{2}^{(1)} | \Phi_{v} \rangle. \quad (6.46)$$

As we can see Eqs. (6.43) and (6.46) are same as Eqs. (6.25) and (6.26) respectively, which were derived earlier.

6.2.3 E1PNC from coupled-cluster theory

The perturbed closed- and open-shell wave functions calculated in the previous section can be used to investigate the PNC effects in the atomic systems. In this section we derive the expression to calculate E1PNC from CC wave functions. From the CC wave function Eq.(6.18)

E1PNC =
$$\langle \tilde{\Psi}_w \| \boldsymbol{D} \| \tilde{\Psi}_v \rangle$$

= $\langle \Phi_w \| e^{T^{\dagger}} (1 + \lambda T^{(1)})^{\dagger} (1 + S + \lambda S^{(1)})^{\dagger} \boldsymbol{D} e^T (1 + \lambda T^{(1)})$
 $(1 + S + \lambda S^{(1)}) \| \Phi_v \rangle.$ (6.47)



Figure 6.8: Some of the leading-order diagrams contributing to the Eq. (6.50). Exchange diagrams are not shown. The zigzag line represent the cluster operators $T_1^{(1)}$ or $S_1^{(1)}$. Line terminated with the circle represent the dipole operator. And the solid line with and without a bar in the middle is to represent the cluster operator $S_2^{(1,1)}$ and $S_2^{(1,0)}$ respectively.

Retaining only the terms which are linear in λ , we get

E1PNC =
$$\langle \Phi_w \| e^{T^{\dagger}} (1+S)^{\dagger} \mathbf{D} e^T (T^{(1)} + S^{(1)} + T^{(1)}S) + e^{T^{\dagger}} (T^{(1)} + S^{(1)} + T^{(1)}S)^{\dagger} \mathbf{D} e^T (1+S) \| \Phi_v \rangle.$$
 (6.48)

Using the commutation relation of the cluster-operators and the expression of the dressed dipole operator

$$\bar{D} = e^{T^{\dagger}} \boldsymbol{D} e^{T}, \qquad (6.49)$$

the E1PNC can further be written as

$$E1PNC = \langle \Phi_w \| \bar{D} (T^{(1)} + S^{(1)} + T^{(1)}S) + (T^{(1)} + S^{(1)} + T^{(1)}S)^{\dagger} \bar{D} + S^{\dagger} \bar{D} (T^{(1)} + S^{(1)} + T^{(1)}S) + (T^{(1)} + S^{(1)} + T^{(1)}S)^{\dagger} \bar{D}S \| \Phi_v \rangle.$$
(6.50)

The diagrammatic representation of Eq. (6.50) is obtained by using Wick's theorem. Some of the leading diagrams are shown in Fig. 6.8.

6.3 Two-valence systems

As mentioned earlier, there very few investigations on the CCT of two-valence systems. There are few applications [114, 115] and these too are at the unperturbed CC level. The properties calculations using perturbed CC of two-valence systems has not been attempted. The atomic properties like E1PNC amplitude [38, 39, 40, 28, 41, 15] and the atomic EDM have important consequences in fundamental physics. It is therefore important to implement

perturbed CC method and carry out precise theoretical calculations. In this section we derive the perturbed CC equations and discuss the procedure to calculate E1PNC of two valence systems.

6.3.1 Perturbed CC equations

As mentioned in the one-valence case, in presence of the PNC perturbation Hamiltonian the wave operator in the Bloch equation is separated as

$$\Omega = \Omega + \lambda \Omega_{\rm PNC}. \tag{6.51}$$

In the CCT, for two-valence atomic systems

$$\Omega = e^{T} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right),$$

$$\Omega_{\text{PNC}} = e^{T} \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}} \right) + e^{T} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right).$$
(6.52)

 $S^{(1,0)}$ and $S^{(1,1)}$ are the unperturbed and perturbed cluster operators, respectively, of the one-valence part. Similarly, $S^{(2,0)}$ and $S^{(2,1)}$ are the two-valence cluster operators of the unperturbed and perturbed atomic systems. Using Eq. (6.52) in the Bloch equation (6.30)

$$\left[e^{T} \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}} \right) + e^{T} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right), H_{0} \right] P = \left[V e^{T} \left(T^{(1)} + S^{(1,1)} + S^{(2,0)} + \frac{1}{2} S^{(1,1)^{2}} \right) + V e^{T} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) + H_{\text{PNC}} e^{T} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) - e^{T} \left(T^{(1)} + S^{(1,1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}} \right) W - e^{T} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) W \right] P.(6.53)$$

Using Eqs. (6.33) and (6.34) in Eq. (6.53) and removing e^T from both



Figure 6.9: Representation of the single and double perturbed cluster operators contributing at the level of two-valence perturbed CC.

sides of the equation we get

$$\left[\left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right) + T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right), H_0 \right] P = \left[\bar{V} \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right) + \bar{V} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right) + \bar{H}_{PNC} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right) - \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right) W - T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right) W \right] P.(6.54)$$

The CC equation is obtained by projecting Eq. (6.54) with the excited determinant $\langle \Phi_{vw}^{pq} |$. This equation contains both connected and disconnected terms, after the Wick's theorem is applied. Retaining only the connected terms, different terms in Eq. (6.54) are simplified in the following way.

$$\langle \Phi_{vw}^{pq} | \left[T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}, H_0 \right]_{\text{conn}} | \Phi_{vw} \rangle = \\ \langle \Phi_{vw}^{pq} \{ \left(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right) H_0 \} - \{ H_0(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}) \} | \Phi_{vw} \rangle,$$

$$(6.55)$$

as no contraction is possible with $T^{(1)}$ and contribute to the CC equation of $S^{(2,1)}$. For the same reason

$$\left\langle \Phi_{vw}^{pq} \right| \left[T^{(1)} (1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}, H_0 \right]_{\text{conn}} \left| \Phi_{vw} \right\rangle = 0.$$
 (6.56)

Similarly, for other terms

$$\langle \Phi_{vw}^{pq} | \bar{V} \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right)_{\text{conn}} | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} | \{ \bar{V} (S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}) \} | \Phi_{vw} \rangle.$$
(6.57)

$$\langle \Phi_{vw}^{pq} | \bar{V}T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right)_{\text{conn}} | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} | \{ \bar{V}T^{(1,1)} (1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}) \} | \Phi_{vw} \rangle.$$
(6.58)

$$\langle \Phi_{vw}^{pq} | \bar{H}_{PNC} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right)_{conn} | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} | \{ \overline{H}_{PNC} (S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}) \} | \Phi_{vw} \rangle, \qquad (6.59)$$

as H_{PNC} alone does not contribute to the $S^{(2,1)}$.

$$\langle \Phi_{vw}^{pq} | \left(T^{(1)} + S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2} \right)_{\text{conn}} W | \Phi_{vw} \rangle = \langle \Phi_{vw}^{pq} \{ (S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}) W \} | \Phi_{vw} \rangle,$$
 (6.60)

$$\langle \Phi_{vw}^{pq} | \left(T^{(1)} + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2} \right)_{\text{conn}} W | \Phi_{vw} \rangle = 0, \qquad (6.61)$$

as $T^{(1)}$ does not contract with W to give $S^{(2,1)}$. Using Eqs. (6.55) - (6.61) in Eq. (6.54) we get the perturbed coupled-cluster equation for two-valence atoms in the form

$$\langle \Phi_{vw}^{pq} | \{ \overline{H_N(S^{(1,1)} + S^{(2,1)} + \frac{1}{2}S^{(1,1)^2}} \} + \{ \overline{H_NT^{(1,1)}(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2}S^{(1,0)^2}}) \}$$

$$= \langle \Phi_{vw}^{pq} \{ (S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}) H_{\text{eff}} \} - \{ \overline{H}_{\text{PNC}} (S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}) \} | \Phi_{vw} \rangle,$$
(6.62)

where we used the relation, $\bar{H}_{\rm N} = H_0 + \bar{V}$, for normal- ordered Hamiltonian.



Figure 6.10: Some of the leading order diagrams contributing to the E1PNC for two-valence systems.

6.3.2 E1PNC from coupled-cluster

Using CC initial and final wave functions of two-valence atoms, $|\tilde{\Psi}_i\rangle$ and $|\tilde{\Psi}_f\rangle$, the expression of E1PNC is

E1PNC =
$$\langle \tilde{\Psi}_{f} \| D \| \tilde{\Psi}_{i} \rangle$$
,
= $\sum_{j,k} c_{j}^{f*} c_{k}^{i} \langle \Phi_{j} \| e^{T^{\dagger}} (1 + \lambda T^{(1)})^{\dagger} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} + \lambda (S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}}) \right)^{\dagger} De^{T} (1 + \lambda T^{(1)})$
 $\left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} + \lambda (S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}}) \right) \| \Phi_{k} \rangle.$
(6.63)

Retaining the terms which are first-order in λ , we get

$$\begin{split} \mathrm{E1PNC} &= \langle \tilde{\Psi}_{f} \| D \| \tilde{\Psi}_{i} \rangle = \sum_{j,k} c_{j}^{f^{*}} c_{k}^{i} \langle \Phi_{j} \| \\ e^{T^{\dagger}} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right)^{\dagger} D e^{T} \left(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}} \right) + \\ e^{T^{\dagger}} T^{(1)^{\dagger}} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right)^{\dagger} D e^{T} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) + \\ e^{T^{\dagger}} \left(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^{2}} \right)^{\dagger} D e^{T} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) + \\ e^{T^{\dagger}} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right)^{\dagger} D e^{T} T^{(1)} \\ \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^{2}} \right) \| \Phi_{k} \rangle. \end{split}$$

$$(6.64)$$

Introducing the dressed electric dipole operator, $\bar{D} = e^{T^{\dagger}} D e^{T}$, above equation can be written in the form

$$E1PNC = \sum_{j,k} c_j^{f^*} c_k^i \langle \Phi_j \|$$

$$\left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right)^{\dagger} \bar{D} \left(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}\right) +$$

$$T^{(1)^{\dagger}} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right)^{\dagger} \bar{D} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right) +$$

$$\left(S^{(1,1)} + S^{(2,1)} + \frac{1}{2} S^{(1,1)^2}\right)^{\dagger} \bar{D} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right) +$$

$$\left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right)^{\dagger} \bar{D} T^{(1)} \left(1 + S^{(1,0)} + S^{(2,0)} + \frac{1}{2} S^{(1,0)^2}\right) \|\Phi_k\rangle.$$
(6.65)

This is the expression of E1PNC for two-valence atoms using CC wave function. In the above equation, the terms with one-order in the cluster operator are expected to be the leading order terms. The second largest contribution is expected from the terms which have two cluster operators. The terms with three or more cluster operators are expected to contribute less. The diagrams contributing to the leading and next to the leading order terms are shown in Fig. 6.10. The coefficients $c_j^{f^*}$ and c_k^i are the eigen vectors of the effective Hamiltonian matrix.

6.4 Summary of the results

In this section we discuss results calculated using perturbed coupled-cluster method. In particular, we discuss the dipole polarizibility results in the case of some of the inert-gases. However, we implement the method to calculate E1PNC as well, the results are given in the next chapter. For the polarizibility calculation we employed the Gaussian type basis functions for which the convergence parameters α and β were give in chapter II.

Table 6.1: The dipole polarizibility of the ground state of neutral rare-gas atoms. The values listed are in atomic units.

Contributions	Ne	Ar	Kr	Xe
${T_1^{(1)}}^\dagger D$	2.7108	11.3330	17.2115	27.7427
$T_1^{(1)\dagger} D T_1^{(0)}$	0.0771	0.0486	0.0429	-0.1495
$T_1^{(1)\dagger} D T_2^{(0)}$	-0.0703	-0.8264	-1.2721	-2.3286
$T_2^{(1)\dagger} D T_1^{(0)}$	-0.0004	-0.0001	0.0002	0.0027
${T_2^{(1)}}^{\dagger} D T_2^{(0)}$	0.0053	0.2490	0.0439	0.0786
Total(CCSD)	2.7225	10.8041	16.0264	25.3459
Approx. triples	2.7281	10.7360	16.0115	25.2974
Exp. values ^a	$2.670 {\pm} 0.005$	11.070(7)	17.075	27.815

^a Reference [155].

The results from our dipole polarizibility calculations of Ne, Ar, Kr and Xe are presented in Table. 6.1. For this we have used the CC expression Eq. (6.16). As mentioned earlier, the dressed dipole operator, \overline{D} , is a non terminating series of the closed-shell cluster operators $T^{(0)}$. For the present calculations we consider the leading terms in $T^{(1)\dagger}\overline{D}$. That is, we use the approximation

$$T^{(1)\dagger}\overline{D} \approx T_1^{(1)\dagger} \left[D + DT_1^{(0)} + DT_2^{(0)} \right] + T_2^{(1)\dagger} \left[DT_2^{(0)} + DT_1^{(0)} \right].$$
 (6.66)

As evident from the above equation, the dipole polarizibility calculations with relativistic CCT involve two sets of cluster amplitudes. These are the $T^{(0)}$ and $T^{(1)}$ cluster amplitudes. The doubles unperturbed cluster amplitudes $T_2^{(0)}$ are found to be larger in magnitude than the singles $T_1^{(0)}$. However, in the case of perturbed clusters $T_1^{(1)}$ is larger than the doubles. The reason for this is the one-body nature of the perturbation.

In Table. 6.1 we give individual contributions from all the CC terms in Eq. (6.66). The first term $T^{(1)\dagger}D$ subsumes contributions arising from Dirac-Fock

and random phase approximation. We can thus expect this term to have the most dominant contribution, as it has only one order of cluster amplitudes and that too the dominant cluster operators. This is evident from Table. 6.1, which shows that the contribution from $T^{(1)\dagger}D$ is far larger than the others. The next two dominant contributions are expected to be $T_1^{(1)\dagger}DT_2^{(0)}$ and $T_1^{(1)\dagger} D T_1^{(0)}$. This is attributed to the reason mentioned earlier, i.e. $T_1^{(1)}$ and $T_2^{(0)}$ are larger than $T_2^{(1)}$ and $T_1^{(0)}$ respectively. Based on the same argument, the least contributing term hence is $T_2^{(1)\dagger} DT_1^{(0)}$. The same pattern is observed in the Table. 6.1. Contribution from the approximate triples cluster amplitudes can be derived from table, and it is about 0.2%, 0.6%, 0.09% and 0.19%respectively for Ne, Ar, Kr and Xe. Our total value of 2.7281 for Ne is within the 2% discrepancy with respect to the experimental data. The deviations are even large in the case of Ar, Kr and Xe, these are respectively about 3.3%, 6.2% and 9.1%. One pattern discernible in the results is the better agreement between the $T^{(1)\dagger}D$ results and experimental data. The large errors in the results are attributed to the approximation in Eq. (6.66) and partly to the basis set.

Chapter 7

*E*1*PNC* from coupled-cluster theory

In the previous three chapters we described the CCT based methods we have developed to calculate wave functions and properties. The main goal of these developments is to compute E1PNC, the observable effect of PNC in atoms: one-valence and two-valence systems. In this chapter we present the analysis of the E1PNC results from computations based on the methods developed so far. In the first section, we discuss the NSD E1PNC results of one-valence atoms and ions, computed using first-order MBPT and coupled-cluster. The results of E1PNC for two-valence atoms are then described in Sec. II.

7.1 E1PNC of one-valence atoms and ions

We have chosen Cs, Fr, Ba⁺ and Ra⁺ as one-valence systems of interest for NSD E1PNC computations. These are the few atoms and ions which have been studied previously, and hence theoretical results are available in the literature. The spin-orbitals employed in the calculations are of the Gaussian type orbitals generated using even tempered scheme and optimized as described in the Chapter. II. The basis parameters of Ba⁺ are given in Chapter. II and for Cs, Fr and Ra⁺ the parameters are given in Table. 7.1 of this chapter. Our E1PNC results of Cs and Fr are tabulated in Table. 7.2. For the Ba⁺ and Ra⁺ ions the results are presented in the Tables . 7.3 and 7.4 respectively. For comparison the results from other theoretical works are also listed.

For atomic Cs, the DF results of E1PNC for the $F = 3 \rightarrow F = 3$, $F = 4 \rightarrow F = 4$, $F = 4 \rightarrow F = 3$ and $F = 3 \rightarrow F = 4$ transitions are 2.011, 2.289, 5.000 and 5.774 respectively. These compare well with the values of 1.908, 2.173, 4.746 and 5.481 from the previous work of Johnson and collaborators [30]. The small deviations may be attributed to the form of the spin-orbital used in the two calculations. In the current study, we have used Gaussian type orbitals, whereas Johnson and collaborators [30] used B-

Atom	Symmetry	α_0	β	Basis function
\mathbf{Cs}	s	0.00721	2.8600	33
	p	0.00755	2.8520	30
	d	0.00653	2.9740	28
\mathbf{Fr}	s	0.00568	2.5300	39
	p	0.00645	2.7890	36
	d	0.00933	2.7790	34
	f	0.00899	2.7250	29
Ra^+	s	0.00625	2.9800	34
	p	0.00715	2.9550	30
	d	0.00700	2.5700	27
	f	0.00695	2.6940	23

Table 7.1: Basis set parameters, α_0 and β , used in the E1PNC calculations for Cs, Fr and Ra atomic systems.

spline as basis functions to generate the spin-orbitals. As its shown in the table, our first-order MBPT results of the first two transitions are close to that of Ref. [30]. It is, however, significantly different for remaining two transitions. The CC results from our calculations are also very different from Ref. [30]. The discrepancies between the two results arise from the different atomic many-body methods used. The results of Ref. [30] are obtained by using random-phase approximation, which forms only a part of the many-body effects incorporated in our CC based theory.

For the atomic Fr we could find only one NSD E1PNC data in the literature, and it is from the work of Porsev and Kozlov [31]. They have, in particular, studied the $7s_{1/2}F = 4 \rightarrow 7s_{1/2}F = 5$ transition. Our DF value of 43.16 is $\approx 3.8\%$ lower than the value reported in the work of Porsev and Kozlov [31]. However, there is a large difference, $\approx 10\%$, between the first-order MBPT result form our work and the total result of Ref. [31]. This is expected as their total result comprise of the DF and core polarization effects. The CC result from our calculation is closer to their results, our result is $\approx 6\%$ lower.

There are a few theoretical results of Ba⁺ ion in literature. However, like in atomic Cs none of these are based on CCT. The results of Sahoo and collaborators [34] are from using the third-order MBPT. Whereas the other works, of Molhotra and collaborators [32] and Geetha and collaborators [33], are computations based on configuration interaction. For all the transitions, DF contributions listed in the previous works and therefore, we compare total results. The sign of MBPT and CCT results from the present work is consistent with the results in Ref. [34].

For the magnitude of E1PNC, MBPT results from the present work are
Transition		E1PNC	Other works	
	MBPT		CCT	
	DF	Total		
Cs $(I = 7/2)$				
$\langle 7s_{1/2}, F = 3 \ \boldsymbol{D} \ 6s_{1/2}, F = 3 \rangle$	2.011	2.060	4.905	$2.249^{\rm a}$
$\langle 7s_{1/2}, F = 4 \ \boldsymbol{D} \ 6s_{1/2}, F = 4 \rangle$	2.289	2.338	5.583	2.560^{a}
$\langle 7s_{1/2}, F = 4 \ \boldsymbol{D} \ 6s_{1/2}, F = 3 \rangle$	5.000	4.819	8.073	$6.432^{\rm a}$
$\langle 7s_{1/2}, F = 3 \ \boldsymbol{D} \ 6s_{1/2}, F = 4 \rangle$	5.774	5.662	9.968	7.299^{a}
$\mathbf{Fr} \left(\mathbf{I} = 0 / 2 \right)$				
(T = 9/2) $\langle 7s_{1/2}, F = 5 \mathbf{D} 7s_{1/2}, F = 4 \rangle$	43.16	44.15	45.84	$49.10^{\rm b}$

Table 7.2: Nuclear spin-dependent E1PNC reduced matrix element for the atoms ¹³³Cs and ²¹¹Fr. The values listed are in units of $i \times 10^{-12} \mu'_W$.

^a Reference[30]. ^b Reference[31].

Table 7.3: Nuclear spin-dependent E1PNC reduced matrix element for the ions ${}^{135/137}\text{Ba}^+$ and ${}^{139}\text{Ba}^+$. The values listed are in units of $i \times 10^{-14} \mu'_W$.

Transition		Others		
	MI	MBPT		
	DF	Total		
$^{135/137}$ Ba ⁺ (I = 3/2)				
$\langle 5d_{3/2}, F = 3 \ \boldsymbol{D} \ 6s_{1/2}, F = 2 \rangle$	90.554	96.299	84.890	$62.1^{\rm a},$
				97.18^{b}
$\langle 5d_{3/2}, F = 2 \ \boldsymbol{D} \ 6s_{1/2}, F = 1 \rangle$	-90.230	-94.699	-81.741	-89.40^{b}
$\langle 5d_{5/2}, F = 3 \ \boldsymbol{D} \ 6s_{1/2}, F = 2 \rangle$	0.100	3.116	10.078	$1.37^{\rm b},$
				-8.2^{c}
$\langle 5d_{5/2}, F = 2 \ \boldsymbol{D} \ 6s_{1/2}, F = 1 \rangle$	0.056	1.526	4.820	$-4.6^{\rm c}$
$^{139}\mathrm{Ba^{+}}\ (I=7/2)$				
$\langle 5d_{3/2}, F = 3 \ \boldsymbol{D} \ 6s_{1/2}, F = 3 \rangle$	100.850	98.619	88.682	103.57^{b}
$\langle 5d_{3/2}, F = 2 \ \boldsymbol{D} \ 6s_{1/2}, F = 3 \rangle$	-98.398	-105.818	-93.012	$-105.55^{\rm b}$
$\langle 5d_{5/2}, F = 2 \ \boldsymbol{D} \ 6s_{1/2}, F = 3 \rangle$	0.044	1.792	5.763	0.608^{b}

^a Reference[32]. ^b Reference[34]. ^c Reference[33].

Transition	E1PNC				
	ME	CCT			
	DF	Total			
$225 \text{Ra}^+ (I = 1/2) \langle 6d_{3/2}, F = 2 \ \boldsymbol{D} \ 7s_{1/2}, F = 1 \rangle$	-856.804	-910.554	$-812.982^{a},$ 991.75 ^b		
²²³ Ra ⁺ ($I = 3/2$) $\langle 6d_{3/2}, F = 3 \ \boldsymbol{D} \ 7s_{1/2}, F = 2 \rangle$	-1013.785	-1083.778	$-968.837^{\rm a},$ $1173.45^{\rm b}$		
$\langle 6d_{3/2}, F = 2 \ \boldsymbol{D} \ 7s_{1/2}, F = 1 \rangle$	1010.229	1076.207	$886.318^{\rm a}, -1017.49^{\rm b}$		
$\langle 6d_{5/2}, F = 3 \ \boldsymbol{D} \ 7s_{1/2}, F = 2 \rangle$	-1.329	-20.157	$50.514^{\rm a}, \\ -17.52^{\rm b}, \\ -63.5^{\rm c}$		
$^{229}\text{Ba}^+$ $(I = 5/2)$					
$\langle 6d_{3/2}, F = 2 \ \boldsymbol{D} \ 7s_{1/2}, F = 3 \rangle$	-404.345	-435.761	$-313.266^{a}, 325.94^{b}$		
$\langle 6d_{3/2}, F = 2 \ \boldsymbol{D} \ 7s_{1/2}, F = 2 \rangle$	-1058.120	-1068.074	$-927.788^{\rm a},$		
$\langle 6d_{5/2}, F = 2 \ \boldsymbol{D} \ 7s_{1/2}, F = 3 \rangle$	-0.039	-6.487	1147.73^{b} $18.510^{a},$ -5.12^{b}		

Table 7.4: Nuclear spin-dependent E1PNC reduced matrix element for the ions 225 Ra⁺, 223 Ra⁺ and a229 Ra⁺. The values listed are in units of $i \times 10^{-14} \mu'_W$.

^a Present work. ^b Reference[34]. ^c Reference[33].

close to the results of Sahoo and collaborators [34]. As the basis function employed in both the calculations are same, the observed small deviation could arise from the difference in the order of residual Coulomb interaction incorporated in the two calculations. Interestingly, the CC results for all the transitions involving the state $5d_{3/2}$ are lower in magnitude than MBPT. However, these are higher for the transitions which involve the state $5d_{5/2}$. A similar pattern is also observed in the results obtained from the computations with the CI method. The CC results of $5d_{5/2}F = 3 \rightarrow 6s_{1/2}F = 2$ and $5d_{5/2}F = 2 \rightarrow 6s_{1/2}F = 1$ transition from the present work are 10.078 and 4.820, respectively. These are close to the to the CI results of -8.2 and -4.6from the work of Geetha and collaborators [33]. However, as we notice the signs are opposite. It is evident from Table. 7.3, there is large difference

Table 7.5:	Nuclear	spin-depend	lent E1P	NC	reduced	matrix	element	for	Yb.
All the val	ues listed	are in units	of $i \times 1$	0^{-11}	μ'_W .				

Transition	Our r	esults	Other works		
	MBPT	CCT			
¹⁷¹ Yb $(I = 1/2)$					
$\langle {}^{3}D_{1}, F = 1/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	-0.257	-0.019	$-1.2238^{\rm a}, -1.375^{\rm b}$		
$\langle {}^{3}D_{1}, F = 3/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	-0.181	-0.008	$0.8654^{\rm a}, -0.970^{\rm b}$		
¹⁷³ Yb $(I = 5/2)$					
$\langle {}^{3}D_{1}, F = 3/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	1.503	0.064	$-1.2108^{\rm a}, 1.410^{\rm b}$		
$\langle {}^{3}D_{1}, F = 5/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	-0.528	-0.022	$-0.4237^{\rm a}, -0.495^{\rm b}$		
$\langle {}^{3}D_{1}, F = 7/2 \ \boldsymbol{D} \ ^{1}S_{0}, F = 5/2 \rangle$	-1.518	-0.065	$1.2231^{\rm a}, -1.425^{\rm b}$		

^a Reference[28]. ^b Reference[29].

between the results from MBPT and CCT when the transitions involve $5d_{5/2}$.

For the Ra⁺ ion, unlike the case of Ba⁺, signs of the first-order MBPT results of transitions involving the $6d_{3/2}$ state from the present study are opposite to the results of Sahoo and collaborators [34]. The signs are, however, consistent for the transitions which have $6d_{5/2}$ as the final state. The CC results, however, show the opposite pattern for all the transitions. Magnitude wise CC results exhibit the similar trend as in Ba⁺.

7.2 E1PNC of two-valence atoms

In this section, we present the E1PNC results of the two-valence atomic systems, ¹⁷¹Yb and ¹⁷³Yb. The basis set parameters used in the calculation are given in the Table. 2.8 of Chapter. II. The E1PNC results from our calculations along with previous theoretical results are listed in the Table. 7.5. It evident from the table, we have chosen the ${}^{1}S_{0} \rightarrow {}^{3}D_{1}$ transition, for different combinations of the allowed hyperfine states. One important consequence of this choice is that the diagonalization of the effective Hamiltonian matrix is not required as the model space does not have multiple states with the same total angular momentum J.

The MBPT and CC results from the present work have the same sign as the results of Porsev and collaborators [29]. However, there is a mismatch of sign for the $\langle {}^{3}D_{1}, F = 3/2 \| \boldsymbol{D} \| {}^{1}S_{0}, F = 1/2 \rangle$, $\langle {}^{3}D_{1}, F = 3/2 \| \boldsymbol{D} \| {}^{1}S_{0}, F = 5/2 \rangle$ and $\langle {}^{3}D_{1}, F = 7/2 \| \boldsymbol{D} \| {}^{1}S_{0}, F = 5/2 \rangle$ transitions between the results in Ref. [28] and Ref. [29]. But in terms of magnitude the two results are very close to

Table 7.6: MBPT E1PNC results for Yb, contributions from the one-body (1b), two-body (2b), Hermitian conjugate of one-body (1bhc) and Hermitian conjugate of two-body (2bhc) terms. All the values listed are in units of $i \times 10^{-11} \mu'_W$.

Transition	MBPT results				
	1b	2b	1bhc	2bhc	
¹⁷¹ Yb $(I = 1/2)$					
$\langle {}^{3}D_{1}, F = 1/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	-0.1506	0.0099	-0.115	-0.0007	
$\langle {}^{3}D_{1}, F = 3/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	-0.1065	0.0070	-0.0814	-0.0005	
173 Yb $(I = 5/2)$					
$\langle {}^{3}D_{1}, F = 3/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	0.8822	-0.0578	0.6740	0.0040	
$\langle {}^{3}D_{1}, F = 5/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	-0.3087	0.0202	-0.2359	-0.0014	
$\langle {}^{3}D_{1}, F = 7/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	-0.8912	0.0584	-0.6809	-0.0041	

Table 7.7: CCT E1PNC results for Yb, contributions from the one-body (1b), two-body (2b), Hermitian conjugate of one-body (1bhc) and Hermitian conjugate of two-body (2bhc) terms. All the values listed are in units of $i \times 10^{-11} \mu'_W$.

		~ ~ ~ ~ ~				
Transition	CCT results					
	0.011054105					
	1b	2b	1bhc	2bhc		
181						
171 Yb $(I = 1/2)$						
$\langle {}^{3}D_{1}, F = 1/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	0.0004	-0.0108	-0.0011	0.0007		
$\langle {}^{3}D_{1}, F = 3/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 1/2 \rangle$	0.0003	-0.0076	-0.0008	0.0005		
$(-1)^{-1}^{-1}^{-1}^{-1}^{-1}^{-1}^{-1}^{-1}$	0.0000	0.00.0	0.0000	0.0000		
170						
173 Yb $(I = 5/2)$						
$\sqrt{{}^{3}D_{1}} F = 3/2 \ \boldsymbol{D} \ ^{1}S_{0} F = 5/2 $	-0.0021	0.0632	0.0066	-0.0039		
$ D_1, I - 0/2 D D_0, I - 0/2/$	0.0021	0.0002	0.0000	0.0000		
$\langle {}^{3}D_{1}, F = 5/2 \ \boldsymbol{D} \ {}^{1}S_{0}, F = 5/2 \rangle$	0.0007	-0.0221	-0.0023	0.0014		
$/^{3}D = E - 7/2 \ D \ ^{1}S = E - 5/2 \rangle$	0 0022	0.0638	0.0068	0.0030		
$ D_1, T - T/2 \ D \ S_0, T = 3/2 $	0.0022	-0.0058	-0.0008	0.0059		

each other. As it is evident from the Table. 7.5, our MBPT results of 173 Yb for all the transitions in good agreement with the results from the two previous works. For 171 Yb the same transitions, however, show the large deviations.

As its shown in the Figs. 2.8 and 6.10 of the previous chapters, using MBPT and CC respectively, the E1PNC diagrams can be separated into one-((a) and (b)) and two-body ((c) - (l)) types. The individual contributions from these, and also from the corresponding Hermitian conjugate terms are given in the Tables. 7.6 and 7.7 using MBPT and CC method respectively. As evident from the tables, CC and MBPT contributions from the two-body terms (2b and 2bhc) are very close to each other. However, the CC results from the one-body terms (1b and 1bhc) are two, in some cases three, orders of magnitude less the corresponding MBPT results. This is also reflected in the Table. 7.5, where the total E1PNC results using CC method is in general two orders of magnitude less than the MBPT results. Unravelling the reason require a detailed analysis and shall be addressed in future.

Chapter 8 Future directions

In the current thesis, we have developed an efficient and favorably known atomic many-body method, the coupled-cluster, for closed-, one-, and twovalence atomic systems. Furthermore, the method is used to study some of the atomic properties such as correlation and excitation energies, hyperfine structure constants, electric dipole transition amplitudes, dipole polarizibility and parity-violation observable E1PNC. Our results, in many cases, are compatible with the other theoretical results, and in some cases even better. However, there are lot more scope to improve the accuracy of the results further. As a future work, we shall be working in the following areas:

As we have mentioned in the Introduction chapter, unlike the case NSI E1PNC, the NSD E1PNC has not been studied in a great detail. There are few calculations and that too are not with using the methods like coupledcluster. There is certainly room for a systematic study of the same in the high-Z atoms, in view of the search of nuclear anapole moment.

The precise theoretical study of the properties for two-valence systems is lacking. A comprehensive and systematic analysis of the same using the CC method shall be the next aim in the future. In this connection, the nonlinear terms in CC equation should be taken in to account.

At the level of properties calculation for the closed-shell case, in particular for correlation energy and dipole polarizibility, we have examined the contributions from approximate triples cluster amplitudes. These are discussed in the previous chapters of the thesis. At the level of CC equations, however, we have used CCSD approximation, in which cluster operators are restricted up to one- and two-body types only. As a future work, we would like incorporate the higher excitation cluster amplitudes, such as triples and quadrupoles.

As reported by the Kozlov and collaborators [22] for PNC in atomic Cs, Breit correction contribute approximately about 1%. Our next future goal is, therefore, to incorporate the Breit interaction in CC formulation. So that the accuracy of our results can be improved further.

The quantum electrodynamic (QED) effects, such as self-energy and vac-

uum polarization, also play an important role in the case of heavy atoms. Systematic inclusion and a quantitive analysis of the same is considered to be next goal of the future work.

Appendix A Matrix element of H_{PNC}

The matrix elements of $H_{\rm PNC}$ are calculated in the hyperfine states $|\gamma(JI)FM_F\rangle$. This is essential as the property of interest is the transition probability arising from $H_{\rm PNC}^{\rm NSD}$, the nuclear spin-dependent component of the Parity nonconserving interaction Hamiltonian. In the coupled state $|\gamma(JI)FM_F\rangle$, J is the total angular momentum quantum number of the electrons, I is the nuclear spin quantum number, and F is the total angular momentum (F = I + J) referred as the hyperfine quantum number. Using the Eq. (1.18)

$$\langle \gamma(JI)FM_F|H_{\rm PNC}^{\rm NSD}|\gamma'(J'I')F'M'_F\rangle$$

$$= \frac{G_{\rm F}\mu'_w}{2\sqrt{2}I} \langle \gamma(JI)FM_F|\sum_i \boldsymbol{\alpha}_i \cdot \boldsymbol{I}\rho_{\rm N}(r)|\gamma'(J'I')F'M'_F\rangle,$$

$$= \frac{G_{\rm F}\mu'_w}{2\sqrt{2}I} (-1)^{J'+I+F+1} \delta(F,F')\delta(M_F,M_{F'}) \left\{ \begin{array}{cc} J & J' & 1\\ I' & I & F \end{array} \right\}$$

$$\times \langle \gamma'J\|\sum_i \boldsymbol{\alpha}_i\rho_{\rm N}(r)\|\gamma'J'\rangle \langle I\|\boldsymbol{I}\|I'\rangle.$$

$$(A.1)$$

In the last step, the matrix elements are converted into uncoupled states. The advatange is, only the electronic component of the reduced matrix element require computation. The remaining angular factors can be evaluated separately and these are just multiplying factors. The reduced matrix element of the nuclear spin operator, in the above equation, is

$$\langle I \| \boldsymbol{I} \| I' \rangle = \delta(I, I') \sqrt{(2I+1)I(I+1)}.$$
 (A.2)

The reduced matrix element of α in terms of CSFs can be reduced to single electron matrix elements as

$$\langle \gamma J \| \sum_{i} \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) \| \gamma' J' \rangle = d_{ab}^{k} (JJ') \langle \gamma j_{a} \| \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) \| \gamma' j_{b} \rangle,$$

$$= d_{ab}^{k} (JJ') \langle \gamma (l_{a}s_{a}) j_{a} \| \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) \| \gamma' (l_{b}s_{b}) j_{b} \rangle,$$
 (A.3)

where $|(l_b s_b) j_b\rangle$ are single electron ls coupled states and $d^k_{ab}(J, J')$ is the angular coefficient. For determinantal states the expression of the matrix is the similar, it is without the angular factor.

Single electron matrix element is then calculated using the relativistic form, Eq(2.9), of the single-electron wave function

$$\langle \gamma(l_a s_a) j_a | \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) | \gamma'(l_b s_b) j_b \rangle = \int \psi_a^{\dagger}(\boldsymbol{r}) \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) \psi_b(\boldsymbol{r}) d^3 r,$$

$$= \int_0^{\infty} dr \int d\Omega \begin{pmatrix} P_a \chi_{\kappa_a m_a}(\hat{\boldsymbol{r}}) \\ i Q_a \chi_{-\kappa_a m_a}(\hat{\boldsymbol{r}}) \end{pmatrix}^{\dagger} \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \begin{pmatrix} P_b \chi_{\kappa_b m_b}(\hat{\boldsymbol{r}}) \\ i Q_b \chi_{-\kappa_b m_b}(\hat{\boldsymbol{r}}) \end{pmatrix} \rho_{\mathrm{N}}(r),$$

$$= i \int_0^{\infty} dr \int d\Omega \left[P_a Q_b \chi_{\kappa_a m_a}^* \boldsymbol{\sigma} \chi_{-\kappa_b m_b} - Q_a P_b \chi_{-\kappa_a m_a}^* \boldsymbol{\sigma} \chi_{\kappa_b m_b} \right] \rho_{\mathrm{N}}(r).$$
(A.4)

The matrix element is nonzero only for orbitals which is nonzero in the nuclear region. The transition matrix elements of $H_{\rm PNC}$ between the orbitals $|ns_{1/2}\rangle$ and $|n'p_{1/2}\rangle$ are then the most dominant. The next is the transition matrix between the states $|ns_{1/2}\rangle$ and $|n'p_{3/2}\rangle$. And, the other matrix elements are practically equal to zero.

A.1 $\langle ns_{1/2}|H_{\rm PNC}|n'p_{1/2}\rangle$

For better representation of the spin-orbitals the radial part, unlike in the previous subsection, is denoted as $\psi_n \kappa$. And, the spin-angular part, like in the earlier expressions are $\chi_{\kappa m}$. For shorter expression the functional dependences are not written explicitly. Using Eq.(A.4), the matrix element can be written as

$$\langle ns_{1/2} | \boldsymbol{\alpha} \rho_{\rm N}(r) | n' p_{1/2} \rangle = i \int_0^\infty dr \int d\Omega \left[P_n Q_{n'} \rho_{\rm N} \chi^*_{-11/2} \boldsymbol{\sigma} \chi_{-11/2} - Q_n P_{n'} \rho_{\rm N} \chi^*_{11/2} \boldsymbol{\sigma} \chi_{11/2} \right].$$
(A.5)

The angular integrals in Eq.(A.5) are further evaluated using the following relations for the spin-angular function $\chi_{\kappa m}$.

$$\chi_{\kappa m} = \sqrt{\frac{l+m+1/2}{2l+1}} Y_l^{m-1/2} \begin{pmatrix} 1\\0 \end{pmatrix} + \sqrt{\frac{l-m+1/2}{2l+1}} Y_l^{m+1/2} \begin{pmatrix} 0\\1 \end{pmatrix}$$

for $j = l+1/2$, and
$$\chi_{\kappa m} = -\sqrt{\frac{l-m+1/2}{2l+1}} Y_l^{m-1/2} \begin{pmatrix} 1\\0 \end{pmatrix} + \sqrt{\frac{l+m+1/2}{2l+1}} Y_l^{m+1/2} \begin{pmatrix} 0\\1 \end{pmatrix}$$

for $j = l-1/2$. (A.6)

Using Eq.(A.6), the angular integral in the first term on the right hand side of Eq.(A.5) is

$$\int d\Omega \chi^*_{-11/2} \boldsymbol{\sigma} \chi_{-11/2} = \int d\Omega \left[\left\{ Y^0_0 \begin{pmatrix} 1\\0 \end{pmatrix} \right\}^{\dagger} \begin{pmatrix} 1&0\\0&-1 \end{pmatrix} \left\{ Y^0_0 \begin{pmatrix} 1\\0 \end{pmatrix} \right\} \right]$$
$$= \int d\Omega Y^{0*}_0 Y^0_0 = 1.$$
(A.7)

Similarly, the angular integral in the second term

$$\int d\Omega \chi_{11/2}^* \boldsymbol{\sigma} \chi_{11/2} = \int d\Omega \left[\left\{ -\frac{1}{\sqrt{3}} Y_1^0 \begin{pmatrix} 1\\0 \end{pmatrix} + \frac{2}{\sqrt{3}} Y_1^1 \begin{pmatrix} 0\\1 \end{pmatrix} \right\}^\dagger \begin{pmatrix} 1&0\\0&-1 \end{pmatrix} \right] \\ \left\{ -\frac{1}{\sqrt{3}} Y_1^0 \begin{pmatrix} 1\\0 \end{pmatrix} + \frac{2}{\sqrt{3}} Y_1^1 \begin{pmatrix} 0\\1 \end{pmatrix} \right\} \right] \\ = \int d\Omega \left[\frac{1}{3} Y_1^{0*} Y_1^0 - \frac{2}{3} Y_1^{1*} Y_1^1 \right] = -\frac{1}{3}.$$
(A.8)

In deriving Eqs.(A.7) and (A.8) we have used the orthonormality relation for the spherical harmonics, $\int Y_l^m Y_{l'}^{m'} d\Omega = \delta_{mm'} \delta_{ll'}$. Using Eqs.(A.7) and (A.8) in Eq.(A.5), the matrix element is then

$$\langle ns_{1/2} | \boldsymbol{\alpha} \rho_{\mathrm{N}}(r) | n' p_{1/2} \rangle = i \int_0^\infty dr \left[P_n Q_{n'} + \frac{1}{3} Q_n P_{n'} \right] \rho_{\mathrm{N}}.$$
(A.9)

This is the expression of the most dominant matrix element. The expression of the corresponding hermitian cojugate matrix element, $\langle n'p_{1/2}|H_{\rm PNC}|ns_{1/2}\rangle$, can also be derived in the similar way to the form

$$\langle n' p_{1/2} | \boldsymbol{\alpha} \rho_{\rm N}(r) | n s_{1/2} \rangle = -i \int_0^\infty dr \left[P_n Q_{n'} + \frac{1}{3} Q_n P_{n'} \right] \rho_{\rm N}.$$
 (A.10)

A.2 $\langle ns_{1/2}|H_{\rm PNC}|n'p_{3/2}\rangle$

Like in the previous case, using Eq.(A.4) we can write

$$\langle ns_{1/2} | \boldsymbol{\alpha} \rho_{\rm N}(r) | n' p_{3/2} \rangle = i \int_0^\infty dr \int d\Omega \left[P_n Q_{n'} \rho_{\rm N} \chi^*_{-11/2} \boldsymbol{\sigma} \chi_{23/2} - Q_n P_{n'} \rho_{\rm N} \chi^*_{11/2} \boldsymbol{\sigma} \chi_{-23/2} \right].$$
 (A.11)

Using Eq.(A.6), the angular integrals are

$$\int d\Omega \chi^*_{-11/2} \boldsymbol{\sigma} \chi_{21/2} = \int d\Omega \left[\left\{ Y^0_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right\}^{\dagger} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \\ \left\{ -\sqrt{\frac{2}{5}} Y^0_2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{3}{5}} Y^1_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\} = 0$$
(A.12)

and

$$\int d\Omega \chi_{11/2}^* \boldsymbol{\sigma} \chi_{-21/2} = \int d\Omega \left[\left\{ -\frac{1}{\sqrt{3}} Y_1^0 \begin{pmatrix} 1\\0 \end{pmatrix} + \sqrt{\frac{2}{3}} Y_1^1 \begin{pmatrix} 0\\1 \end{pmatrix} \right\}^\dagger \begin{pmatrix} 1&0\\0&-1 \end{pmatrix} \right] \left\{ \sqrt{\frac{2}{3}} Y_1^0 \begin{pmatrix} 1\\0 \end{pmatrix} + \frac{1}{\sqrt{3}} Y_1^1 \begin{pmatrix} 0\\1 \end{pmatrix} \right\} = -\frac{2\sqrt{2}}{3}. \quad (A.13)$$

Using Eqs.(A.12) and (A.13) in Eq.(A.11), we get

$$\langle ns_{1/2} | \boldsymbol{\alpha} \rho_{\rm N}(r) | n' p_{3/2} \rangle = i \frac{2\sqrt{2}}{3} \int_0^\infty dr P_{n'} Q_n \rho_{\rm N}.$$
 (A.14)

This is the expression of the other single electron matrix element which contributes to the E1PNC. Similarly we can derive for the corresponding hermitian conjugate matrix element

$$\langle n' p_{3/2} | \boldsymbol{\alpha} \rho_{\rm N}(r) | n s_{1/2} \rangle = -i \frac{2\sqrt{2}}{3} \int_0^\infty dr P_{n'} Q_n \rho_{\rm N}.$$
 (A.15)

Appendix B

Matrix element of dipole operator

The matrix element of the dipole operator between two CSFs of opposite parity, using Wigner-Ekart theorem, is

$$\langle \Phi_k | \boldsymbol{D} | \overline{\Phi}_j \rangle = \langle \gamma(JI) PFM_F | \boldsymbol{D} | \gamma'(J'I') - PF'M'_F \rangle$$

$$= (-1)^{F-M_F} \begin{pmatrix} F & 1 & F' \\ -M_F & q & M'_F \end{pmatrix} \langle \gamma(JI)F|D|\gamma'(J'I')F' \rangle,$$

$$= (-1)^{F-M_F} (-1)^{J+I+F'+1} \delta(I,I')[F,F']^{1/2} \begin{pmatrix} F & 1 & F' \\ -M_F & q & M'_F \end{pmatrix} \times$$

$$\begin{cases} F & 1 & F' \\ J' & I & J \end{cases} \langle \gamma J \| D \| \gamma' J' \rangle.$$

$$(B.1)$$

The reduced matrix element can further be simplified to the spin-orbital level as

$$\langle \gamma J \| D \| \gamma' J' \rangle = d_k^{ab} (J, J') \langle \gamma J_a \| d \| \gamma' J_b \rangle = d_k^{ab} (J, J') \langle \gamma (l_a s_a) J_a \| d \| \gamma' (l_b s_b) J_b \rangle,$$
 (B.2)

where, like in the case $H_{rmPNC}^{\text{NSD}} d_{\dots}^{\dots}$ angular factors and the spin-orbitals as usual are ls coupled states. The explicit expression of the dipole operator matrix element in terms of the spin-orbitals is

$$\langle \gamma(l_a s_a) j_a | \boldsymbol{d} | \gamma'(l_b s_b) j_b \rangle$$

$$= -\int d^3 r \psi_a^{\dagger}(\boldsymbol{r}) \boldsymbol{r} \psi_b(\boldsymbol{r}),$$

$$= -\int_0^{\infty} dr \int d\Omega \begin{pmatrix} P_a \chi_{\kappa_a m_a}(\hat{\boldsymbol{r}}) \\ i Q_a \chi_{-\kappa_a m_a}(\hat{\boldsymbol{r}}) \end{pmatrix}^{\dagger} \begin{pmatrix} \boldsymbol{r} & 0 \\ 0 & \boldsymbol{r} \end{pmatrix} \begin{pmatrix} P_b \chi_{\kappa_b m_b}(\hat{\boldsymbol{r}}) \\ i Q_b \chi_{-\kappa_b m_b}(\hat{\boldsymbol{r}}) \end{pmatrix},$$
(B.3)

Without loss of generality, the z-axis can be considered as the axis of quantization and component of d along the axis is $d_z = d \cos \theta$. The corresponding matrix element is then

$$\langle \gamma(l_a s_a) j_a | d_z | \gamma'(l_b s_b) j_b \rangle = -\int_0^\infty drr(P_a^* P_b + Q_a^* Q_b) \int d\Omega \chi^*_{\kappa_a m_a}(\hat{\mathbf{r}}) \cos \theta \chi_{\kappa_b m_b}(\hat{\boldsymbol{r}})$$
(B.4)

From this expression applying the Wigner-Eckert theorem it is possible to obtain the reduced matrix element. The relations $\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}} \chi_{-\kappa_b m_b} = \chi_{\kappa_b m_b}$, and $(\boldsymbol{\sigma} \cdot \hat{\boldsymbol{r}})^2 = 1$ are used while arriving at the final expression.

A more general and convenient expression is to calculate the matrix element with d defined in terms of C tensor as

$$\mathbf{d} = r\mathbf{C}^1. \tag{B.5}$$

Where, by definition the components of the C-tensor are

$$C_q^k(\theta,\phi) = \sqrt{\frac{4\pi}{2k+1}} Y_q^k(\theta,\phi).$$
(B.6)

In this case, as the dipole operator is defined as function of C-tensor, the Wigner-Eckert theorem can be directly applied. The reduced matrix element is then

$$\langle \gamma(l_a s_a) j_a \| d \| \gamma'(l_b s_b) j_b \rangle = -\int_0^\infty drr(P_a^* P_b + Q_a^* Q_b) \langle \kappa_a \| C^1 \| \kappa_b \rangle, \qquad (B.7)$$

where the reduced matrix element

$$\langle \kappa_a \| \boldsymbol{C}^k \| \kappa_b \rangle = (-1)^{j_a + 1/2} \sqrt{(2j_a + 1)(2j_b + 1)} \begin{pmatrix} j_a & j_b & 1\\ -1/2 & 1/2 & 0 \end{pmatrix} \Pi(l_a + l_b + 1).$$
(B.8)

Here, the parity function is

$$\Pi(l_a + l_b + 1) = \begin{cases} 1 & \text{if } l_a + l_b + 1 \text{ is even} \\ 0 & \text{otherwise} \end{cases}.$$
(B.9)

It more convenient to use the dipole matrix element in Eq. (B.7) than the previous expression. One basic advatage is, it directly computes the reduced matrix element.

Appendix C E1PNC in hyperfine states

In terms of hyperfine states, the H_{PNC} induced dipole transition amplitude between initial and final states $|\Psi_i\rangle$ and $|\Psi_f\rangle$, respectively, is

$$E1PNC = \sum_{n} \left[\frac{\langle (IJ_f)F_f \| D \| (IJ_n)F_n \rangle \langle (IJ_n)F_n \| H_{PNC} \| (IJ_i)F_i \rangle}{E_i - E_n} + \frac{\langle (IJ_f)F_f \| H_{PNC} \| (IJ_n)F_n \rangle \langle (IJ_n)F_n \| D \| (IJ_i)F_i \rangle}{E_f - E_n} \right]. \quad (C.1)$$

Here, the index n represents the intermediate states which are opposite in parity to the initial and final states. Conventionally, I denotes the intermediate states in time-independent perturbation theory but n is used to avoid confusion with nuclear spin I. Using Eqs. (A.1) and (B.1) for the H_{PNC} and dipole matrix elements respectively, the reduced matrix elements in the first term in Eq.(C.1) are

$$\langle (IJ_f)F_f \|D\| (IJ_n)F_n \rangle = \delta(I,I)(-1)^{I+J_n+F_f+1} \sqrt{(2F_f+1)(2F_n+1)} \\ \times \left\{ \begin{array}{cc} F_f & 1 & F_n \\ J_n & I & J_f \end{array} \right\} \langle J_f \|D\| J_n \rangle,$$
 (C.2)

$$\langle (IJ_n)F_n \| H_{\text{PNC}} \| (IJ_i)F_i \rangle = -\frac{G_{\text{F}}\mu'_{\text{w}}}{\sqrt{2I}} \sqrt{3(2F_n+1)(2F_i+1)} \\ \times \left\{ \begin{array}{cc} I & I & 1 \\ J_n & J_i & 1 \\ F_n & F_i & 0 \end{array} \right\} \langle I \| I \| I \rangle \langle J_n \| \alpha \rho_N(r) \| J_i \rangle. (C.3)$$

The 9j in Eq.(C.3) can be simplified to

$$\left\{ \begin{array}{cc} I & I & 1 \\ J_n & J_i & 1 \\ F_n & F_i & 0 \end{array} \right\} = \delta(F_n, F_i)(-1)^{1+I+J_n+F_n} \frac{1}{\sqrt{3(2F_n+1)}} \left\{ \begin{array}{cc} I & I & 1 \\ J_i & J_n & F_n \end{array} \right\}.$$
(C.4)

Similarly, for the second term in Eq.(C.1) the reduced matrix elements are

$$\langle (IJ_f)F_f \| H_{\text{PNC}} \| (IJ_n)F_n \rangle = -\frac{G_F \mu'_w}{\sqrt{2I}} \sqrt{3(2F_f+1)(2F_n+1)} \\ \times \left\{ \begin{array}{cc} I & I & 1 \\ J_f & J_n & 1 \\ F_f & F_n & 0 \end{array} \right\} \langle I \| I \| I \rangle \langle J_f \| \alpha \rho_N(r) \| J_n \rangle (C.5)$$

$$\langle (IJ_n)F_n \|D\| (IJ_i)F_i \rangle = \delta(I,I)(-1)^{I+J_i+F_n+1} \sqrt{(2F_n+1)(2F_i+1)} \\ \times \left\{ \begin{array}{cc} F_n & 1 & F_i \\ J_i & I & J_n \end{array} \right\} \times \langle J_n \|D\| J_i \rangle.$$
 (C.6)

The 9j in Eq.(C.5) is

$$\left\{ \begin{array}{cc} I & I & 1 \\ J_f & J_n & 1 \\ F_f & F_n & 0 \end{array} \right\} = \delta(F_f, F_n)(-1)^{1+I+J_f+F_f} \frac{1}{\sqrt{3(2F_f+1)}} \times \left\{ \begin{array}{cc} I & I & 1 \\ J_n & J_f & F_f \end{array} \right\}.$$
(C.7)

In the case of atomic Yb the $H_{\rm PNC}$ induced dipole transitions of interest are ${}^{1}S_{0} \rightarrow {}^{3}D_{1}$ and ${}^{1}S_{0} \rightarrow {}^{3}D_{2}$. The second, as mentioned else where in the thesis, is an ideal choice to detect nuclear anapole moment as only the $H_{\rm PNC}^{\rm NSD}$ contributes in this case. For the second transition, namely ${}^{1}S_{0} \rightarrow {}^{3}D_{1}$, the values of angular momenta are $J_{i} = 0$, $F_{i} = I$, $J_{n} = 1$, and $J_{f} = 2$. Using these in Eqs(C.2), (C.3), (C.5), and (C.6) and using in Eq.(C.1), after rearranging

$$(\text{E1PNC})_{{}^{1}S_{0}}^{{}^{3}D_{2}} = G_{\text{F}}\mu_{\text{w}}'(-1)^{2F_{f}} \left\{ \begin{array}{c} F_{f} & 1 & I \\ 1 & I & 2 \end{array} \right\} \sqrt{\frac{(2F_{f}+1)(I+1)(2I+1)}{6I}} \\ \sum_{n} \left[\frac{\langle^{3}D_{2} \| \alpha \rho_{N}(r) \| J_{n} = 1 \rangle \langle J_{n} = 1 \| D \|^{1}S_{0} \rangle}{E_{{}^{3}D_{2}} - E_{n}} + \frac{\langle^{3}D_{2} \| D \| J_{n} = 1 \rangle \langle J_{n} = 1 \| \alpha \rho_{N}(r) \|^{1}S_{0} \rangle}{E_{{}^{1}S_{0}} - E_{n}} \right].$$
(C.8)

In a similar way, the expression of the transition amplitude for the ${}^{1}S_{0} \rightarrow {}^{3}D_{1}$ can be derived.

Appendix D

Matrix element of hyperfine operator

D.1 Magnetic dipole hyperfine matrix element

Using Eq. (4.37), the magnetic dipole hyperfine matrix element is

$$\langle \kappa_w | t_q^1(\mathbf{r}) | \kappa_v \rangle = -i\sqrt{2} \langle \kappa_w | \frac{[\boldsymbol{\alpha} \cdot \mathbf{C}_1^{(0)}(\hat{\mathbf{r}})]_q}{cr^2} | \kappa_v \rangle. \tag{D.1}$$

Using the single electron relativistic wave function

$$\langle \kappa_w | t_q^1(\mathbf{r}) | \kappa_v \rangle = \int_0^\infty \frac{dr}{r^2} \int d\Omega$$

$$\begin{pmatrix} P_w \chi_{\kappa_w m_w}(\hat{\mathbf{r}}) \\ i Q_w \chi_{-\kappa_w m_w}(\hat{\mathbf{r}}) \end{pmatrix}^\dagger \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \mathbf{C}_1^{(0)}(\hat{\mathbf{r}}) \\ \boldsymbol{\sigma} \cdot \mathbf{C}_1^{(0)}(\hat{\mathbf{r}}) & 0 \end{pmatrix} \begin{pmatrix} P_v \chi_{\kappa_v m_v}(\hat{\mathbf{r}}) \\ i Q_v \chi_{-\kappa_v m_v}(\hat{\mathbf{r}}) \end{pmatrix},$$

$$= -i\sqrt{2} \int_0^\infty \frac{dr}{r^2}$$

$$\left[i P_w Q_v \langle \kappa_w m_w | \boldsymbol{\sigma} \cdot \mathbf{C}_1^{(0)} | - \kappa_v m_v \rangle - i Q_w P_v \langle -\kappa_w m_w | \boldsymbol{\sigma} \cdot \mathbf{C}_1^{(0)} | \kappa_v m_v \rangle \right].$$

$$(D.2)$$

In the above equation, for the convenience, the angular part of the integral is retained in the form of the matrix element. For the same reason we have also dropped the θ and ϕ dependence of the spherical tensor operator. Using the following relations

$$\langle \kappa_b m_b | \boldsymbol{\sigma} \cdot \mathbf{C}_{kq}^{(0)} | - \kappa_a m_a \rangle = \frac{-\kappa_a - \kappa_b}{k(k+1)} \langle \kappa_b m_b | \mathbf{C}_q^k | - \kappa_a m_a \rangle, \text{ and} \langle -\kappa_b m_b | \boldsymbol{\sigma} \cdot \mathbf{C}_{kq}^{(0)} | \kappa_a m_a \rangle = \frac{\kappa_a + \kappa_b}{k(k+1)} \langle -\kappa_b m_b | \mathbf{C}_q^k | \kappa_a m_a \rangle$$
 (D.3)

for the matrix elements, Eq. (D.2) is simplified to the form

$$\langle \kappa_w | t_q^1(\mathbf{r}) | \kappa_v \rangle = -\frac{\sqrt{2}}{k(k+1)} (\kappa_w + \kappa_v)$$
$$\int_0^\infty \frac{dr}{r^2} \left[P_w Q_v \left\langle \kappa_w m_w | \mathbf{C}_0^1 | - \kappa_v m_v \right\rangle + Q_w P_v \left\langle -\kappa_w m_w | \mathbf{C}_0^1 | \kappa_v m_v \right\rangle \right] (D.4)$$

From the symmetry condition $\langle \kappa_w m_w | \mathbf{C}_0^1 | - \kappa_v m_v \rangle = \langle -\kappa_w m_w | \mathbf{C}_0^1 | \kappa_v m_v \rangle$ and the multipole k = 1, the above hyperfine matrix element is further simplified as

$$\langle \kappa_w | t_q^1(\mathbf{r}) | \kappa_v \rangle = -(\kappa_w + \kappa_v) \int_0^\infty \frac{dr}{r^2} \left(P_w Q_v + Q_w P_v \right) \langle -\kappa_w m_w | \mathbf{C}_0^1 | \kappa_v m_v \rangle.$$
(D.5)

D.2 Electric quadrupole hyperfine matrix element

Using Eq. (4.38), the electric quadrupole hyperfine matrix element is

$$\langle \kappa_w | t_q^2(\mathbf{r}) | \kappa_v \rangle = -\langle \kappa_w | \frac{\mathbf{C}_q^2(\hat{\mathbf{r}})}{r^3} | \kappa_v \rangle.$$
 (D.6)

Using the single electron relativistic wave function and following the same mathematical steps as in the case of magnetic dipole hyperfine matrix elements, we can derive

$$\langle \kappa_w | t_q^2(\mathbf{r}) | \kappa_v \rangle = -\int_0^\infty \frac{dr}{r^3} \left(P_w Q_v + Q_w P_v \right) \langle -\kappa_w m_w | \mathbf{C}_0^2 | \kappa_v m_v \rangle.$$
(D.7)

Where the general matrix element for the spherical tensor operator of rank k and component q follows the relation, using Wigner-Eckart theorem

$$\langle \kappa_b | C_q^k | \kappa_a \rangle = (-1)^{j_b - m_b} \begin{pmatrix} j_b & k & j_a \\ -m_b & q & m_a \end{pmatrix} \langle \kappa_b | | C^k | | \kappa_a \rangle, \qquad (D.8)$$

where, the reduced matrix element $\langle \kappa_b || C^k || \kappa_a \rangle$ is given in Eq. (B.8).

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